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# Is hyperconjugation responsible for the “*gauche* effect” in 1-fluoropropane and other 2-substituted-1-fluoroethanes? †

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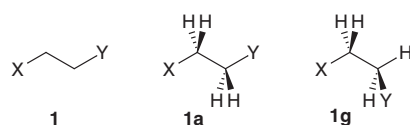
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The energies and geometries of a series of 2-substituted-1-fluoroethanes were computed at the MP2/6-311++G\*\* (6D)/MP2/6-31+G\* level of theory for both the maxima and minima of the rotation about the C–C bond. The results did not support the predictions of a hyperconjugative model, that both 1,2-difluoroethane and 1-chloro-2-fluoroethane would strongly prefer a *gauche* conformation, and that 1-fluoro-2-silylethane would strongly prefer an *anti* conformation. The existence of competing electrostatic interactions between the fluorine and the substituents at C-2 was indicated by the detailed geometries of the *gauche* conformers and by the calculated sensitivity of the *gauche*–*anti* energy differences to the presence of a polar solvent. However, Fourier analyses of the torsional potential energies were wholly consistent with hyperconjugative electron donation into the C–F  $\sigma^*$  orbital contributing to the conformational preferences of these 1-fluoroethanes. Fourier analyses also showed that hyperconjugation contributes to the small variations in C–C and C–F bond lengths and in fluorine atomic charges that were computed. The torsional potential energies, variations in geometry and atomic charge, and sensitivity to solvent were all in accord with the expected ranking of hyperconjugative electron donating ability of bonds to carbon, C–Si > C–H > C–C > C–Cl > C–F.

## Introduction

The name “*gauche* effect” has been given<sup>1–4</sup> to the phenomenon that in 1,2-disubstituted ethanes **1** the *gauche* conformer **1g** is populated to a larger extent than *anti* conformer **1a** when the substituents X and Y are both electronegative atoms such as oxygen or fluorine (Scheme 1). This preference is surprising,

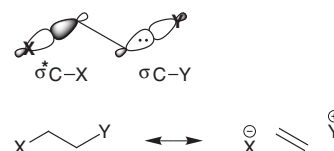


Scheme 1

since both dipole repulsions between electronegative atoms and steric effects should favor the *anti* conformation. A variety of 1-substituted propanes, e.g. **1** (X = CH<sub>3</sub>, Y = Cl, F, OH), are also known to prefer a *gauche* conformation.<sup>5–9</sup>

The *gauche* effect has been attributed primarily to  $\sigma$ -hyperconjugation, which can be described equivalently in terms of donor–acceptor orbital interactions or resonance structures (Scheme 2).<sup>10–14</sup> More specifically, the most stable conformation of a 1,2-disubstituted ethane has been postulated to place the best  $\sigma$ -donor bond *anti* to the best  $\sigma$ -acceptor bond.

Evidence for the importance of hyperconjugative electron donation into C–F  $\sigma^*$  orbitals in neutral fluorocarbons has come from a variety of calculations and experiments.<sup>15</sup> Therefore, if the hyperconjugative explanation of the *gauche* effect is correct, the preferred conformations of 2-substituted-1-



Scheme 2 Schematic orbital and resonance depictions of hyperconjugative electron donation from C–Y into  $\sigma^*$  of C–X.

fluoroethanes can be used to establish the electron donating ability of the bond to the substituent at C-2, relative to the C–H bonds at this carbon. For example, since 1-fluoropropane is known to prefer a *gauche* conformation,<sup>16–18</sup> the hyperconjugative explanation of the *gauche* effect implies that the C<sup>2</sup>–H  $\sigma$  bonds donate more strongly than the C<sup>2</sup>–C<sup>3</sup>  $\sigma$  bond into the C<sup>1</sup>–F  $\sigma^*$  orbital.

The question of whether a C–H bond is a stronger or weaker hyperconjugative  $\sigma$ -donor than a C–C bond has long been controversial.<sup>19,20</sup> Attempts have been made to correlate C–H *versus* C–C hyperconjugation with other experimental observables such as <sup>13</sup>C NMR chemical shifts.<sup>21–23</sup> However, the question might appear to have been settled by the known preference of 1-fluoropropane for the *gauche* conformation. Moreover, the energy difference between the *gauche* and *anti* conformations should reflect the energy difference between C–H and C–C hyperconjugative donation into the C–F  $\sigma^*$  orbital.

Unfortunately, other explanations of the preferred conformation of 1-fluoropropane are possible. For instance, dipole-induced dipole attraction between the fluorine atom and the methyl group might significantly stabilize the *gauche* conformation; or bond-bending of the sort described by Wiberg<sup>24</sup> might play an important role. Therefore, it is of some importance to establish how large a role hyperconjugation actually does play in determining the preferred conformation of 1-fluoropropane and other 2-substituted-1-fluoroethanes.

The hypothesis that hyperconjugative electron donation

† Table S1 and  $z$ -matrices from MP2/6-31+G\* optimizations are available as supplementary data. For direct electronic access see <http://www.rsc.org/suppdata/p2/1999/1719>, otherwise available from BLDSC (SUPPL. NO. 57570, pp. 18) or the RSC Library. See Instructions for Authors available via the RSC web page (<http://www.rsc.org/authors>).

into C–F  $\sigma^*$  orbitals plays a dominant role in governing the conformational behavior of 2-substituted-1-fluoroethanes can be tested by considering carbon–substituent bonds that can be confidently assigned as either much stronger or much weaker donors than C–H. For example, the C–F bonds in 1,2-difluoroethane should be much weaker donors than the C–H bonds. In the *gauche* conformer, a C–H bond is positioned to donate into each of the C–F  $\sigma^*$  orbitals; whereas in the *anti* conformer only the C–F  $\sigma$  bonds can act as electron donors. Thus, the hypothesis that hyperconjugation controls conformation unequivocally predicts that the *gauche* conformer should be strongly favored. Experiments<sup>25–30</sup> and calculations<sup>24,30–38</sup> both indicate that 1,2-difluoroethane does, in fact, adopt a *gauche* geometry, thus providing support for hyperconjugative control of conformation.

At the other extreme from 1,2-difluoroethane is 1-fluoro-2-silylethane. C–Si bonds are known to be highly effective electron donors in both carbocations<sup>39</sup> and neutral compounds,<sup>40</sup> much stronger donors than either C–C or C–H. The hyperconjugative model then leads to the unequivocal prediction that in 1-fluoro-2-silylethane the *anti* conformation, in which the C–Si bond acts as the donor to the C–F  $\sigma^*$  orbital, should be strongly preferred to the *gauche* conformation, in which a C–H bond is the donor.

Since the torsional potential energy of 1-fluoro-2-silylethane has not, to the best of our knowledge, previously been calculated, we undertook the computational study described in this paper, in order to test the hypothesis that the *anti* conformation would be preferred. We found, instead, that in 1-fluoro-2-silylethane, the preference for an *anti* conformation is so small that at some levels of theory the *gauche* conformer is actually predicted to be lower in energy.<sup>41</sup> This finding led us to perform additional calculations in order to understand more fully what factors actually do determine the conformational preferences of 2-substituted-1-fluoroethanes. Herein we report the results of these computational studies.

## Calculations

Initial optimizations were carried out at HF/6-31G\* and were followed by vibrational analyses to determine whether each stationary point was a minimum (*anti* and *gauche* conformers) or a transition state (*syn* and eclipsed structures). Subsequent geometric refinement was carried out at MP2/6-31+G\*, followed by single-point calculations at MP2/6-311++G\*\*(6D). This procedure is very similar to one used successfully by Wiberg and coworkers in a related study.<sup>31</sup> Atomic charges were obtained from the MP2/6-31+G\* density using Weinhold's natural population analysis.<sup>42</sup> The effect of a solvent was simulated using the IPCM continuum reaction field model,<sup>43</sup> with the relative permittivity set to 20 and the isodensity contour set to 0.0004 electrons per cubic bohr and using the gas-phase geometries.<sup>31</sup> All calculations were carried out using GAUSSIAN94.<sup>44</sup>

Consideration was given to whether the MP2/6-311++G\*\*(6D) calculations were sufficient for obtaining accurate relative energies of the various 2-substituted-1-fluoroethane conformers, or if a better treatment of electron correlation was necessary. The changes that occurred between the MP2/6-311++G\*\*(6D) relative energies and the corresponding HF/6-311++G\*\*(6D) relative energies were modest. In no case did the order of conformer energies change. No energy change exceeded 0.55 kcal mol<sup>–1</sup>, and most of the differences were considerably smaller, averaging less than 0.3 kcal mol<sup>–1</sup>. The relatively small size of the MP2 corrections suggested that a higher-level treatment of electron correlation was not required in order to achieve good accuracy.

In order to confirm the adequacy of the MP2 calculations, we carried out MP4SDTQ/6-311++G\*\*(6D) single point calculations on 1,2-difluoroethane, the molecule for which

**Table 1** Relative energies (kcal mol<sup>–1</sup>)

Compound	Conformer ( $\tau$ ) <sup>b</sup>	MP2/6-31+G*		MP2/6-311++G**(6D) <sup>a</sup>	
		Gas	IPCM <sup>c</sup>	Gas	IPCM <sup>c</sup>
<b>DFE</b>	<i>anti</i> (180°)	0.50	1.81	0.80	1.91
	<i>ecl</i> (124.6°)	2.83	4.05	3.38	4.40
	<i>gauche</i> (71.5°)	0.00	0.00	0.00	0.00
	<i>syn</i> (0°)	8.57	8.35	8.38	8.21
<b>CFE</b>	<i>anti</i> (180°)	0.00	0.42	0.00	0.36
	<i>ecl</i> (120.3°)	4.01	3.89	4.33	4.22
	<i>gauche</i> (67.5°)	0.63	0.00	0.51	0.00
	<i>syn</i> (0°)	8.20	7.24	8.21	7.40
<b>FP</b>	<i>anti</i> (180°)	0.38	0.00	0.28	0.00
	<i>ecl</i> (119.8°)	3.85	3.58	3.89	3.69
	<i>gauche</i> (62.3°)	0.00	0.03	0.00	0.07
	<i>syn</i> (0°)	5.26	5.21	5.27	5.28
<b>FSE</b>	<i>anti</i> (180°)	0.00	0.00	0.00	0.00
	<i>ecl</i> (115.3°)	4.09	4.07	4.16	4.11
	<i>gauche</i> (53.2°)	0.39	0.77	0.50	0.88
	<i>syn</i> (0°)	2.65	3.21	2.99	3.55

<sup>a</sup> Single-point calculations at the MP2/6-31+G\* optimized geometries.

<sup>b</sup> XCCY dihedral angle in degrees. <sup>c</sup> Solution environment simulated using the IPCM model in GAUSSIAN94, with the relative permittivity at  $\epsilon = 20$  and the electron density contour at 0.0004 electrons per cubic bohr.

the largest changes occurred on going from HF to MP2. As expected, the MP4SDTQ relative energies fell between the HF and MP2 relative energies, but were much closer to the MP2 energies. On going from MP2 to MP4SDTQ, the largest change in relative energy occurred for the *syn* conformer, which decreased by 0.4 kcal mol<sup>–1</sup>, but this change represented only 5% of the *syn*–*anti* energy difference. The other changes were all less than 0.2 kcal mol<sup>–1</sup>. Thus it seemed highly unlikely that higher levels of correlation treatment would alter the results derived from the MP2 calculations in any significant manner, and so no further such calculations were deemed necessary.

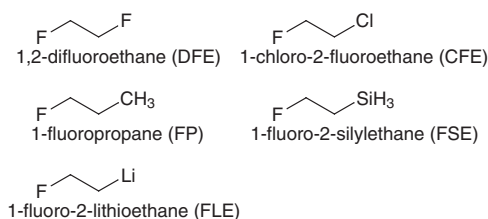
Analytical expressions for torsional potential energy functions were determined using the MP2/6-311++G\*\*(6D)/MP2/6-31+G\* energies for four conformers of each compound: the *anti* minimum ( $C_s$  or  $C_{2h}$ ), the *gauche* minimum ( $C_1$  or  $C_2$ ), the *syn* transition state ( $C_s$  or  $C_{2v}$ ), and the remaining eclipsed transition state ( $C_1$  or  $C_2$ ). The four energies and corresponding torsional angles were then used to solve for the four parameters  $V_0$ – $V_3$  in eqn. (1).

$$V(\theta) = V_0 + \frac{1}{2}V_1 \cos(\theta) + \frac{1}{2}V_2 \cos(2\theta) + \frac{1}{2}V_3 \cos(3\theta) \quad (1)$$

Similar Fourier decompositions of contributors to torsional potential energies have been used successfully by Pople and coworkers.<sup>45</sup> The same technique was used by us to analyze the contributors to the geometric and atomic charge variations correlated with torsion about the C<sup>1</sup>–C<sup>2</sup> bond.

## Results

Table 1 lists the calculated relative energies of 1,2-difluoroethane (**DFE**), 1-chloro-2-fluoroethane (**CFE**), 1-fluoropropane (**FP**), and 1-fluoro-2-silylethane (**FSE**) (Scheme 3) at the four



**Scheme 3**

**Table 2** Gas-phase Fourier coefficients for torsional potential energies (eqn. (1)) (kcal mol<sup>-1</sup>)<sup>a</sup>

Compound	$V_0$	$V_1$	$V_2$	$V_3$
<b>DFE</b>	2.77	3.16	3.63	4.42
<b>CFE</b>	3.05	3.06	2.11	5.15
<b>FP</b>	2.23	0.75	1.08	4.24
<b>FSE</b>	2.06	-0.42	-1.13	3.41

<sup>a</sup> For MP2/6-311++G\*\*(6D) energies computed at the MP2/6-31+G\* optimized geometries.

**Table 3** IPCM (solution) Fourier coefficients for torsional potential energies (eqn. (1)) (kcal mol<sup>-1</sup>)<sup>a,b</sup>

Compound	$V_0$	$V_1$	$V_2$	$V_3$
<b>DFE</b>	3.20	1.55	3.73	4.75
<b>CFE</b>	2.75	1.99	2.26	5.05
<b>FP</b>	2.15	1.13	0.99	4.15
<b>FSE</b>	2.24	0.22	-0.94	3.33

<sup>a</sup> Solution environment simulated using the IPCM model in GAUSSIAN94, with the relative permittivity at  $\epsilon=20$  and the electron density contour at 0.0004 electrons per cubic bohr. <sup>b</sup> For MP2/6-311++G\*\*(6D) energies computed at the MP2/6-31+G\* optimized geometries.

unique stationary points on the torsional potential energy function. Calculations were performed for molecules both in the gas phase and in a polarizable medium having a relative permittivity of 20, characteristic of acetone. The IPCM continuum-based model used for the latter calculations is known to describe solvent effects on conformational equilibria of 1,2-disubstituted ethanes quite well, at least in non-associating aprotic solvents such as acetone.<sup>31,43,46</sup> The Fourier decompositions of the torsional potential energy functions, both with and without solvent, are given in Tables 2 and 3.

Many previous experimental and computational studies have addressed the conformational behavior of **DFE**.<sup>24–38,47–50</sup> The numerous calculations all concur that the *gauche* conformer is preferred to the *anti* in the gas phase by 0.5–1.0 kcal mol<sup>-1</sup>.<sup>24,30–38</sup> The highest level of calculation previously applied is probably the G2(MP2) study by Wiberg and coworkers.<sup>31</sup> They found a *gauche*–*anti* energy difference of 0.75 kcal mol<sup>-1</sup>, in excellent agreement with the value of 0.80 kcal mol<sup>-1</sup> reported in Table 1.

Gas-phase NMR measurements have given 0.83 kcal mol<sup>-1</sup><sup>25</sup> for this energy difference, in excellent agreement with the calculated values. Older electron diffraction studies gave slightly larger values in the 1–2 kcal mol<sup>-1</sup> range.<sup>26–29</sup> However, vibrational spectroscopy has been used to obtain a gas-phase energy difference of  $0.8 \pm 0.1$  kcal mol<sup>-1</sup>, in excellent agreement with both the best calculated and the gas-phase NMR values.<sup>30</sup>

Wiberg has previously calculated solvent effects on the *gauche*–*anti* energy difference in **DFE**, also using the polarizable continuum model.<sup>31</sup> The present findings are, not surprisingly, in essentially exact agreement with the results of Wiberg's earlier study. The calculated ratios are in reasonably good agreement with experimental determinations of the *gauche*–*anti* energy difference in solution<sup>31,48,49</sup> as discussed in detail by Wiberg *et al.*<sup>31</sup>

A number of previous studies have also examined the torsional potential energies of **CFE**.<sup>31,51,52</sup> Again, our calculated energy difference of 0.51 kcal mol<sup>-1</sup> favoring *anti* over *gauche* is in excellent agreement with the G2(MP2) value of Wiberg and coworkers.<sup>31</sup> Both calculations are in reasonable agreement with the gas-phase experimental values of  $0.82 \pm 0.08$  kcal mol<sup>-1</sup> derived from vibrational spectroscopy<sup>51</sup> and 0.44 kcal mol<sup>-1</sup> derived from electron diffraction.<sup>52</sup>

The torsional potential energy function for **FP** has been

**Table 4** Bond lengths<sup>a</sup> and atomic charges<sup>b</sup>

Compound	Conformer ( $\tau$ )	$r(\text{C–C})/\text{\AA}$	$r(\text{C–F})/\text{\AA}$	F Charge (au)
<b>DFE</b>	<i>anti</i> (180°)	1.5134	1.4103	-0.4019
	<i>ecl</i> (124.6°)	1.5212	1.4118	-0.4048
	<i>gauche</i> (71.5°)	1.5012	1.4060	-0.4014
	<i>syn</i> (0°)	1.5445	1.3981	-0.3876
<b>CFE</b>	<i>anti</i> (180°)	1.5133	1.4105	-0.4024
	<i>ecl</i> (120.3°)	1.5261	1.4118	-0.4046
	<i>gauche</i> (67.5°)	1.5072	1.4051	-0.4011
	<i>syn</i> (0°)	1.5440	1.3997	-0.3913
<b>FP</b>	<i>anti</i> (180°)	1.5114	1.4157	-0.4116
	<i>ecl</i> (119.8°)	1.5273	1.4191	-0.4148
	<i>gauche</i> (62.3°)	1.5114	1.4178	-0.4159
	<i>syn</i> (0°)	1.5364	1.4173	-0.4119
<b>FSE</b>	<i>anti</i> (180°)	1.5092	1.4197	-0.4133
	<i>ecl</i> (115.3°)	1.5305	1.4177	-0.4121
	<i>gauche</i> (53.2°)	1.5145	1.4197	-0.4131
	<i>syn</i> (0°)	1.5230	1.4268	-0.4133
<b>FLE</b>	<i>anti</i> (180°)	1.4833	1.4628	-0.4629

<sup>a</sup> Obtained from MP2/6-31+G\* optimization. <sup>b</sup> Obtained via natural population analyses (NPA) at MP2/6-31+G\*.

**Table 5** Fourier coefficients for C–C bond lengths (Å)<sup>a</sup>

Compound	$V_0$	$V_1$	$V_2$	$V_3$
<b>DFE</b>	1.5176	0.0097	0.0227	0.0214
<b>CFE</b>	1.5211	0.0087	0.0152	0.0220
<b>FP</b>	1.5210	0.0062	0.0059	0.0188
<b>FSE</b>	1.5204	-0.0009	-0.0087	0.0147

<sup>a</sup> Obtained from MP2/6-31+G\* optimizations.

determined experimentally by microwave spectroscopy.<sup>16</sup> Our calculations agree with experiment that the *gauche* conformer is favored, and our calculated energy difference of 0.28 kcal mol<sup>-1</sup> is in close agreement with the experimental value of 0.37 kcal mol<sup>-1</sup>. The measured barrier heights of 3.47 kcal mol<sup>-1</sup> (*ecl* = eclipsed) and 4.19 kcal mol<sup>-1</sup> (*syn*) can be compared to our calculated values 3.89 kcal mol<sup>-1</sup> and 5.27 kcal mol<sup>-1</sup>. The experimental values for the barrier heights have much larger error limits than those of the *gauche*–*anti* energy difference. The *gauche*–*anti* energy difference calculated by us is in good agreement with previously calculated values.<sup>17,18</sup>

Fuchs *et al.*<sup>53</sup> have pointed out that hyperconjugation should also influence bond lengths and charge densities. The stronger the hyperconjugation between the C–Y donor bond at C-2 and the C–X acceptor bond at C-1, the shorter should be the bond between C-1 and C-2 and the longer should be the bonds between C-2 and the donor and between C-1 and the acceptor. The negative charge on fluorine should also increase as a result of the hyperconjugative interaction (*cf.* Scheme 2). These predictions were largely borne out by calculations for 1,2-dimethoxyethane and **DFE**. Predictions regarding the C–C bond lengths were supported by substantial data from the Cambridge crystallographic data file.<sup>53</sup>

In order to ascertain possible effects of hyperconjugation on geometries we wanted to compute accurately the optimized bond lengths. The MP2/6-31G\* level of theory is known to give geometries that are in close agreement with experiment.<sup>54</sup> An additional set of diffuse functions was used in our MP2/6-31+G\* geometry optimizations, since such functions are known to be important for the description of lone pairs. The C–C and C–F bond lengths and the charges on fluorine at the various stationary points are given in Table 4, and the corresponding Fourier decompositions appear in Tables 5, 6 and 7.

Experimental structural data from electron diffraction, microwave spectroscopy and vibrational spectroscopy are



**Table 6** Fourier coefficients for C–F bond lengths (Å)<sup>a</sup>

Compound	$V_0$	$V_1$	$V_2$	$V_3$
<b>DFE</b>	1.4066	−0.0133	−0.0049	0.0011
<b>CFE</b>	1.4069	−0.0124	−0.0037	0.0016
<b>FP</b>	1.4178	0.0001	−0.0025	0.0015
<b>FSE</b>	1.4200	0.0052	0.0066	0.0019

<sup>a</sup> Obtained from MP2/6-31+G\* optimizations.**Table 7** Fourier coefficients for fluorine atomic charges (au)<sup>a</sup>

Compound	$V_0$	$V_1$	$V_2$	$V_3$
<b>DFE</b>	−0.3995	0.0137	0.0095	0.0006
<b>CFE</b>	−0.4004	0.0106	0.0071	0.0005
<b>FP</b>	−0.4141	−0.0008	0.0047	0.0005
<b>FSE</b>	−0.4128	−0.0006	−0.0010	0.0006

<sup>a</sup> Obtained from natural population analyses (NPA) at MP2/6-31+G\*.

available for some of the compounds for which we have performed calculations.<sup>26,30,51,55,56</sup> Microwave<sup>55</sup> and vibrational<sup>30</sup> spectroscopy of **DFE** have independently given a value of 71.0° for the F–C–C–F dihedral angle in the *gauche* conformer, in very close agreement with our MP2/6-31+G\* value of 71.5°. The microwave-derived values of 1.494 Å and 1.390 Å for, respectively, the C–C and C–F bond lengths are also in close agreement with the present results.<sup>55</sup> Electron diffraction yields 71.3° for the dihedral angle and 1.503 Å and 1.389 Å for the C–C and C–F bond lengths of **DFE**.<sup>26</sup>

The F–C–C–Cl dihedral angle in **CFE** has been experimentally determined as 68°,<sup>51</sup> in excellent accord with the calculated value of 67.5°. Microwave spectroscopy has also been used to study **FP**,<sup>57</sup> and the experimentally determined C–C–C–F dihedral angle for the *gauche* conformer of 62.6° is in excellent accord with our calculated value of 62.3°. Furthermore, comparison of our calculated C<sup>1</sup>–C<sup>2</sup> and C–F bond lengths with the experimental values of 1.506 Å and 1.390 Å again shows the high degree of agreement with experiment that is expected from this level of theory.

## Discussion

### Preferred conformations of 2-substituted-1-fluoroethanes

Although MP2/6-31G\* calculations find a 0.73 kcal mol<sup>−1</sup> preference for the *gauche* over the *anti* conformer of **FSE**,<sup>41</sup> the results of both MP2/6-31+G\* and MP2/6-311++G\*\*(6D) calculations support the hyperconjugative prediction that the *anti* conformation should be preferred. However, even at these two higher levels of theory, the preference for *anti* over *gauche* is only 0.4–0.5 kcal mol<sup>−1</sup>. This finding is quite surprising, because, as discussed in the Introduction, the difference between C–Si and C–H hyperconjugative electron donation in **FSE** is expected to be quite substantial.

Similarly, the known preference of **DFE** for the *gauche* conformer is not as great as the hyperconjugative model might lead one to expect. In the *gauche* conformer each of the two sets of C–H bonds can donate into each C–F σ\* orbital; whereas, in the *anti* conformation, donation into each C–F σ\* orbital can only occur from a C–F bond. Therefore the preference for the *gauche* conformer should be much more pronounced in **DFE** than in **FP**, where the *gauche*–*anti* preference is determined by the difference between C–H and C–CH<sub>3</sub> donation into a single C–F σ\* orbital, rather than by the difference between C–H and C–F donation into two C–F σ\* orbitals. However, as shown in Table 1, the energetic preference for *gauche* over *anti* is only slightly larger in **DFE** than in **FP**.

Finally, hyperconjugation would predict **CFE** to prefer a *gauche* conformation, much like **DFE**. However, our calcu-

lations show that, instead, **CFE** prefers an *anti* to a *gauche* conformation by about 0.5 kcal mol<sup>−1</sup> in the gas-phase.

It might appear that these comparisons between the qualitative predictions of the hyperconjugative model and the conformational preferences found for **DFE**, **CFE**, **FSE** and **FP** by high quality *ab initio* calculations show that hyperconjugation cannot be the dominant cause of the *gauche* effect. However, it is important to bear in mind that other factors also contribute to these conformational preferences. For instance, what is particularly remarkable about the fact that **DFE** adopts a *gauche* conformation is that this preference exists at all, despite the repulsion between the C–F bond dipoles that favors the *anti* conformer.

In **CFE** the electrostatic repulsion between the C–F and C–Cl bond dipoles is expected to be smaller than the repulsion between the C–F bond dipoles in **DFE**. The decreased electrostatic repulsion should tend to make the *gauche* conformation even more favored in **CFE** than in **DFE**. On the other hand, the hyperconjugative preference for *gauche* would be expected to be weaker in **CFE** than in **DFE**, since a C–Cl bond is both a better electron donor and a weaker electron acceptor than a C–F bond. Thus our finding that the preferred conformation changes from *gauche* in **DFE** to *anti* in **CFE** (Table 1) is presumably due to a decrease in the importance of hyperconjugation in **CFE** compared to **DFE**. The alternative explanation, that a C–Cl bond is a better hyperconjugative electron donor than a C–H bond, seems much less likely.

In **FSE** electrostatic interactions between the C–Si and C–F bonds should also contribute to the potential for torsion about the central C–C bond. However, unlike the case in **DFE**, the Coulombic interaction between the terminal groups in **FSE** should be attractive. Therefore, electrostatic interactions should stabilize the *gauche* relative to the *anti* conformer in the latter compound.

The validity of the hyperconjugative hypothesis thus requires the additional assumption that conformational preferences in **DFE** and **FSE** are small because electrostatic interactions oppose the only slightly larger effects of hyperconjugation.<sup>58</sup> In contrast, although the preference for a *gauche* conformation that is both calculated and observed in **FP** could indicate that C–H is a stronger donor bond than C–C, as already noted, this preference could also be due, wholly or in part, to an electrostatic attraction between the negatively charged fluorine and a polarized C–H bond of the methyl group. Consequently, at least a qualitative indication of the importance of such electrostatic interactions in 2-substituted-1-fluoroethanes is required, in order to validate the hypothesis that hyperconjugative donation into the C–F σ\* orbital actually does play a significant role in determining the preferred conformations of **DFE**, **CFE**, **FSE** and **FP**.

One approach is to examine the size of the dihedral angle in the *gauche* conformers of these molecules. This angle should be less than the idealized value of 60° if there is electrostatic attraction between the fluorine and the *gauche* substituent, greater than 60° if there is repulsion, and about equal to 60° if there is no significant interaction between them. For example, the 72° dihedral angle in *gauche* **DFE** does provide evidence for the existence of substantial repulsion between the two C–F bonds. The 67.5° dihedral angle in **CFE** also indicates significant repulsion between fluorine and chlorine, although of a lesser magnitude than the repulsion between the C–F bonds in **DFE**.

In *gauche* **FSE**, on the other hand, the unusually small dihedral angle of 53° suggests an attraction between fluorine and silicon. An attraction, presumably electrostatic, is also suggested by the finding that the *syn*–*anti* energy difference is much smaller in **FSE** than in any of the other compounds in Table 1.

Finally, the rather unexceptional dihedral angle of 62.3° in the *gauche* conformer of **FP** provides no evidence for an electrostatic interaction between methyl and fluorine in this compound. The size of this dihedral angle thus supports the

argument that the greater ability of a C–H compared to a C–C bond to act as a hyperconjugative electron donor is primarily responsible for the preference for a *gauche* conformation in this compound.

### Solvent effects

Another way to address qualitatively the importance of electrostatics is to consider the effect of solvent, since a polar medium would certainly moderate 1,4-electrostatic interactions but should have very little effect on hyperconjugative interactions. The isodensity polarizable continuum model (IPCM), implemented in GAUSSIAN94,<sup>44</sup> provides a mechanism to study this question. Although the model is approximate, and cannot properly describe cases where specific solute–solvent interactions play an important role, Wiberg and coworkers have shown that this model provides an adequate description of the solvent effects on 1,2-dihaloethanes.<sup>31</sup> Furthermore, for the present application, quantitative accuracy in the calculation of solvent effects is not required; and, in fact, the idealized nature of the IPCM model makes interpretation of the computational results obtained with it particularly straightforward.

The effects of solvent on the torsional potential energy surfaces for **DFE** and **CFE** have already been studied by both computation<sup>31</sup> and experiment.<sup>31,48</sup> In agreement with the earlier findings by Wiberg and coworkers,<sup>31,48</sup> the results in Table 1 show that the preference for a *gauche* conformation in **DFE** increases substantially in the presence of a polar solvent. This observation supports the argument that the gas-phase preference for *gauche* over *anti* is small, not because of a small difference between hyperconjugative donation by C–H and C–F bonds, but rather, because of competition from electrostatic repulsion between the C–F bonds.

Furthermore, the conformational preference of **CFE** changes from *anti* to *gauche* upon going from the gas-phase to a polar environment. Therefore, the preferred conformation of **CFE** in solution, though not in the gas-phase, is that predicted by the hyperconjugative model. The solution behavior again supports the argument that the unexpected conformational preference observed in the gas-phase for **CFE** results from an electrostatic repulsion between fluorine and chlorine that counteracts the hyperconjugative preference for a *gauche* conformation.

The computational results in Table 1 also show that the preference of **FSE** for an *anti* structure would be strengthened in a polar solvent that reduces the intramolecular electrostatic attraction between fluorine and silicon. The existence of this electrostatic effect explains why the calculated preference for the *anti* conformation in the gas-phase is much smaller than would have been expected solely on the basis of the difference in hyperconjugative donor ability between C–H and C–Si.

Finally, the results in Table 1 indicate that a polar solvent would wipe out the small gas-phase preference for a *gauche* conformation in **FP**. This computational result strongly suggests that an electrostatic attraction between fluorine and methyl really does contribute to the gas-phase preference for a *gauche* conformation in **FP**, both computed and found experimentally. This finding also indicates that the dihedral angle of 62.3° in the *gauche* conformation of **FP** does not really imply the absence of an electrostatic attraction. Instead, this angle apparently represents a compromise between steric and electrostatic effects.

### Fourier analysis of the torsional potential energy surfaces

The obvious contribution of more than one factor to the preferred conformations of 2-substituted-1-fluoroethanes makes even qualitative analyses of the relative sizes of the contributions of these factors complicated. In order to determine the sizes of these contributions quantitatively, we have performed Fourier analyses of the torsional potential energies of **DFE**, **CFE**, **FSE** and **FP** along the lines originally suggested by

Pople.<sup>45</sup> The Fourier coefficients,  $V_1$ – $V_3$ , in eqn. (1) each represent the size of a different factor that contributes to the relative energies of the various conformers.

The  $V_0$  term is a constant that has no conformational dependence and simply establishes the zero of energy at the preferred conformation. The  $V_1$  term takes its maximal value at 0° (*syn*) and its minimal value at 180° (*anti*). It can therefore be associated with components of the energy that vary with this periodicity. The most obvious contributions that meet this description are the steric and electrostatic interactions between the substituent at C-2 and the fluorine at C-1.  $V_1$  is positive for electrostatic and steric repulsions between them and negative for attractions. Bond-bending strain of the sort described by Wiberg<sup>24</sup> would also presumably exhibit this 1-fold periodicity, and contribute to  $V_1$  with a negative sign, since the bending strain would be at a minimum for a dihedral angle of 0° and at a maximum for a dihedral angle of 180°. Any preference for anti-rather than synperiplanar hyperconjugation would also contribute to the  $V_1$  term.

The  $V_2$  term can be associated with hyperconjugation between the C–F and C–Y bonds. It is at a maximum at 0° and 180°, where the C–F and C–Y bonds in **1** are coplanar, and at a minimum for 90° and 270°, where these bonds are orthogonal. The sign of  $V_2$  depends on whether the bond to the substituent, Y, at C-2 is a better or a worse hyperconjugative donor than the C–H bonds at this carbon.

The  $V_3$  term is positive, since it describes eclipsing interactions. It has its maxima at F–C–C–Y dihedral angles of 0°, 120° and 240° and its minima at 60°, 180° and 300°.

Fourier analyses were carried out for calculations on **DFE**, **CFE**, **FSE** and **FP** in the gas phase and, as an aid to separating electrostatic from steric interactions, also in the presence of a polarizable medium representing a solvent. As discussed earlier, the polarizable medium is expected to moderate the 1,4-intramolecular electrostatic interactions that are present in the  $V_1$  term, but to have relatively little effect on steric contributions to  $V_1$  or on the sorts of interactions represented by the  $V_2$  and  $V_3$  terms. Table 2 lists the Fourier coefficients for the gas-phase, while Table 3 provides the corresponding values for a simulated solution environment.

The  $V_3$  terms are quite similar across all four molecules; and, as expected, these terms are affected only very weakly by the presence of solvent.  $V_3$  is smallest for **FSE**, indicating that the eclipsing interactions, averaged over all three eclipsed conformations, are a little weaker in **FSE** than in the other three molecules. This result can probably be rationalized on the basis of the long C–Si bond. The  $V_3$  term is slightly larger for **CFE** than for **DFE**, presumably as a result of the larger size of chlorine compared to fluorine.

In the gas-phase the  $V_1$  term is much larger for **DFE** and **CFE** than for **FP** or **FSE**. This result is in accord with the large electrostatic repulsion expected between the negatively charged halogen atoms. Furthermore, the large repulsive  $V_1$  terms in the former pair of compounds are reduced by roughly half in the presence of solvent, consistent with a substantial electrostatic contribution to these terms. In solution  $V_1$  for **CFE** is *ca.* one third larger than for **DFE**, probably due to the larger steric demand of chlorine, relative to fluorine.

The  $V_1$  term is fairly small for **FP**, presumably as a consequence of the more or less electroneutral methyl group; but  $V_1$  is still positive and, hence, repulsive. The calculated increase in  $V_1$  in a polar solvent, which disfavors the *syn* and *gauche* structures relative to the *anti*, suggests that a small electrostatic attraction between fluorine and methyl really does exist in the gas-phase, perhaps due to a dipole-induced dipole interaction between them. Steric interactions, which favor the *anti* conformer and do not depend on the solvent, then lead to a slight preference for the *anti* conformer.

The  $V_1$  term is mildly attractive for **FSE** in the gas-phase, consistent with an electrostatic attraction between F and SiH<sub>3</sub>.

Quite reasonably, the attraction is reduced by  $0.6 \text{ kcal mol}^{-1}$  upon inclusion of solvent. This electrostatic attraction is superimposed upon a steric repulsion between F and  $\text{SiH}_3$ , which is why  $V_1$  changes sign in going from the gas-phase to solution.

In terms of the hyperconjugative explanation of the *gauche* effect, the  $V_2$  term is of the greatest interest, since  $V_2$  is associated with the difference in hyperconjugative donor ability between the bond to the substituent, Y, and the bonds to the hydrogen atoms at the same carbon. Positive values of  $V_2$  indicate that C–Y is a weaker donor than C–H, since conformers with  $90^\circ$  and  $270^\circ$  Y–C–C–F dihedral angles are preferred. Negative values, on the other hand, indicate that C–Y is a stronger donor than C–H, since conformers with Y–C–C–F dihedral angles of  $0^\circ$  or  $180^\circ$  are preferred.

The  $V_2$  term is large and positive in **DFE**, positive and slightly smaller in **CFE**, even smaller but still positive in **FP**, and negative in **FSE**. These results imply the following order of  $\sigma$ -donor ability of bonds to carbon: C–Si > C–H > C–C > C–Cl > C–F.

In **DFE**, there is a strong preference for the C–F bonds to be at right angles to each other, so that the C–H bonds can hyperconjugatively donate electron density into the C–F  $\sigma^*$  orbitals. The preference is large for two reasons. First, there are two C–F bonds in **DFE** that can act as electron acceptors; second, C–H bonds are substantially better electron donors than C–F bonds.

**CFE** is similar to **DFE**, except that the bias against Cl being coplanar to F is only a little more than half as strong as that against F–F coplanarity. This change is due to C–Cl bonds being better electron donors and poorer electron acceptors than C–F bonds.

For **FP**, there is also a preference against a coplanar arrangement of the C–CH<sub>3</sub> and C–F bonds, indicating that the C–H bonds at C-2 are better electron donors than the C–C bond. However, the Fourier coefficient  $V_2$  in **FP** is less than half the size of that in **CFE** or **DFE**, for two reasons. One is that there is only one electron accepting group in **FP**, not two as in **CFE** or **DFE**. The other reason is that the difference between the electron donating ability of the C–C and C–H bonds in **FP** is not as large as the difference between the C–Cl and C–H bonds in **CFE** or between the C–F and C–H bonds in **DFE**.

Finally, in **FSE**, the  $V_2$  term has a negative sign, so there is a preference for the C–Si bond to be coplanar with the C–F bond. This preference indicates that the C–Si bond is a better electron donor than a C–H bond. However, it is noteworthy that the magnitude of the preference for C–Si *versus* C–H donation is only about the same size as the preference for C–H *versus* C–C donation in **FP**.

As shown by comparison of the results in Tables 2 and 3, the solvent effects on all the  $V_2$  terms are consistently small. This absence of solvent dependence from the  $V_2$  terms is in accord with their interpretation as reflecting whether C–H or C–Y donation into a C–F  $\sigma^*$  orbital is preferred, rather than these terms having an electrostatic origin.

### Bond lengths and atomic charges

As discussed by Fuchs,<sup>53</sup> the hyperconjugative hypothesis for explaining the *gauche* effect also makes predictions about bond lengths and charge distributions. As the electron donor strength of the C–Y bond in the position *anti* to fluorine increases, the C–C bond should shorten, the C–F bond should lengthen, and the negative charge on fluorine should increase (Scheme 2). Table 4 lists calculated bond lengths and atomic charges for the four conformers of each compound in Table 1.

Calculations were also carried out for the *anti* conformation of 1-fluoro-2-lithioethane (**FLE**). Full torsional analysis was not feasible for this compound, because **FLE** collapses to ethene and lithium fluoride, except when restricted to an *anti*

geometry. However, the C–Li bond is of interest as an even more extreme case of a strong donor than C–Si, and examination of bond lengths and charges in the *anti* conformer of **FLE** provides a means of including this substituent.

The variations in bond lengths that appear in Table 4 are generally very small, in most cases at or beyond the limits of experimental detection; and the changes in fluorine atomic charge are also small. Nonetheless, the differences between them in the *anti* conformers of the molecules in Table 4 appear to be largely in agreement with the hyperconjugative hypothesis and with the expected ordering of the electron donating abilities of the C–Y bonds. For example, the C–Li bond is unambiguously the strongest donor in the series; and in **FLE**, the C–C bond is the shortest, the C–F bond the longest, and the fluorine charge the most negative of all the *anti* conformers in Table 4. At the other extreme is *anti* **DFE**, and the other 2-substituted-1-fluoroethanes in Table 4 fall between these two extremes.

However, bond lengths and atomic charges, like the conformational energies discussed above, are influenced by several factors, making the differences between geometries and charges in the *anti* conformers risky to interpret solely in terms of hyperconjugation. Indeed, perusal of Table 4 shows that most of these differences between the *anti* conformations of the 2-substituted-1-fluoroethanes are also present in the *gauche* conformers. Consequently, these differences between compounds cannot properly be attributed to hyperconjugation.

In addition, the variations of bond lengths with conformation for each of these compounds do not appear to be those expected on the basis of hyperconjugation. For example, based on the hyperconjugative model, changes in length with conformation would be expected to take place with particular prominence for the C–Si bond in **FSE**. Hyperconjugation predicts that the *anti* conformer, in which the C–Si bond can best act as a donor to the C–F  $\sigma^*$  orbital, should have a longer C–Si bond than the *gauche* conformer. However, the observed variation in C–Si bond length is not only small but in the wrong direction; the bond length is  $1.896 \text{ \AA}$  in the *anti* conformer, compared to  $1.898 \text{ \AA}$  in the *gauche* conformer. Furthermore, the C–F bond length of **FSE** is computed to be exactly the same in the *anti* and *gauche* conformers; and, except in the eclipsed conformer, the charges on fluorine are all exactly the same. Neither the bond length variations nor the fluorine charges in **FSE** appear to conform to the pattern expected for hyperconjugative donation from the C–Si bond into the C–F  $\sigma^*$  orbital.

### Fourier analysis of bond length and atomic charge variations

As discussed above in connection with the changes in energy with conformation, appearances can be deceiving, especially when several different factors contribute to the changes in a given quantity. A better test of the predictions of the hyperconjugative model can be sought in a Fourier analysis of the variations in bond lengths and charges that occur as a function of dihedral angle. The effects of interactions between the orbitals of the C–F and C–Y bonds are expected to be at a maximum at  $0^\circ$  and  $180^\circ$  but at a minimum at  $90^\circ$  and  $270^\circ$ , and so the  $V_2$  term of the Fourier expansions should again reflect the consequences of hyperconjugation.

Tables 5, 6 and 7 provide the Fourier coefficients for the variations of the C–C and C–F bond lengths and the fluorine atomic charges. The Fourier coefficients, like the changes in bond lengths and atomic charges to which they are related, are very small. However, both the signs and the relative magnitudes of the  $V_2$  terms are in exact agreement with the predictions of the hyperconjugative argument and with the expected ordering of electron donor ability C–Si > C–H > C–C > C–Cl > C–F, also found in the torsional potential energies. This parallel between the changes in energies on the one hand and geometries and atomic charges on the other is reassuring.



## Summary

Provided that hyperconjugation is the dominant factor in determining the preferred conformations of 1,2-disubstituted ethanes, the greater potency of a C–H bond than a C–C bond as a  $\sigma$ -electron donor is established by the preference of **FP** for a *gauche* conformation. However, the geometries of the *gauche* conformations, solvent effects on the *gauche*–*anti* energy differences, and Fourier analyses of the conformational energies all demonstrate that electrostatic and steric factors also influence the conformational behavior of these compounds. For example, electrostatic repulsions destabilize the *gauche* conformer of **DFE** and are responsible for the *anti* conformation of **CFE** being preferred in the gas-phase. In contrast, electrostatic attractions stabilize the *gauche* conformers of **FSE** and **FP**. Thus, in a solvent as polar as acetone the preference for an *anti* conformation in **FSE** is computed almost to double from that in the gas-phase, and the *gauche* and *anti* conformers of **FP** are predicted to be about equally populated.

Fourier analysis allows the rigorous deconvolution of the various factors influencing the torsional potential energies of 2-substituted-1-fluoroethanes. In this manner it was possible to isolate those variations in not only energy but also bond length and charge which have the two-fold periodicity that is unique to hyperconjugative donor–acceptor orbital interactions in these compounds. The  $V_2$  terms derived for **DFE**, **CFE**, **FSE** and **FP** yield a ranking of  $\sigma$ -donor ability of bonds in the order C–Si > C–H > C–C > C–Cl > C–F. Based on the  $V_2$  coefficient for **FSE**, C–Si is better than C–H as the hyperconjugative donor to a C–F  $\sigma^*$  orbital by approximately 1 kcal mol<sup>–1</sup>; and the  $V_2$  coefficient for **FP** shows that C–H is, in fact, a better hyperconjugative donor than C–C by about the same amount.

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- 58 With **DFE**, **CFE** and **FSE**, hyperconjugation and electrostatics are in conflict and so the observed conformational preference for an *anti* or a *gauche* conformation is small. However, it is also possible to imagine molecules in which the two forces are in agreement. For instance, in the anionic species  $\text{FCH}_2\text{CH}_2\text{BH}_3^-$ , both factors favor the *anti* conformer. Since both the  $\text{BH}_3^-$  group and the fluorine atom bear negative charge, the electrostatic interaction is repulsive

and favors the *anti* conformation. On the other hand, since boron is electropositive, the C–B bond is expected to be a better electron donor than a C–H bond and so hyperconjugation favors the *anti* conformation as well. In agreement with these predictions, MP2/6-311++G\*\*(6D)//MP2/6-31+G\* calculations indicate that the *anti* conformer is preferred over the *gauche* conformer by 5.95 kcal mol<sup>-1</sup>.

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