Conformational analysis, Part 32.† NMR, solvation and theoretical investigation of conformational isomerism in 3-fluorobutan-2-one and 3,3-difluorobutan-2-one

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Received (in Cambridge) 20th April 1999, Accepted 7th June 1999

The solvent and temperature dependence of the ^{1}H and ^{13}C NMR spectra of 3-fluorobutan-2-one (FB) and 3,3-difluorobutan-2-one (DFB) are reported and the $^4J_{HF}$, $^1J_{CF}$ and $^2J_{CF}$ couplings analysed using *ab initio* calculations and solvation theory. The solvent dependence of the IR spectra (carbonyl band) was also measured. In FB, *ab initio* theory at the 6-31G**/MP2 level gives only two energy minima for the *cis* (F–C–C=O 22°) and *trans* (F–C–C=O 178°) rotamers. The *gauche* rotamer was not a minimum in the energy surface. Assuming only the *cis* and *trans* forms, the observed couplings when analysed by solvation theory lead to the energy difference ($E_{cis} - E_{trans}$) between the *cis* and *trans* rotamers of 3.7 kcal mol^{-1} in the vapour phase, decreasing to 2.5 kcal mol^{-1} in CCl$_4$ and to 0.1 kcal mol^{-1} in DMSO. In all solvents used the *trans* rotamer is more stable than the *cis*. The vapour state energy difference compares very well with that calculated [3.67 kcal mol^{-1} including a zero-point energy correction (ZPE)]. In DFB *ab initio* calculations at this level and also at (6-311G**/MP2 and ZPE) gave only one minimum in the potential energy surface corresponding to the *cis* rotamer (C–C–C=O 0°). The ^{1}H and ^{13}C NMR data, $^4J_{HF}$, $^1J_{CF}$ and $^2J_{CF}$ couplings do not change with solvent confirming that there is only one rotamer in solution for DFB, in agreement with the *ab initio* calculations.

Introduction

The discovery that the microwave spectrum of CH$_2$F–COF showed the existence of the *cis* (F–C–C=O 0°) and *trans* (F–C–C=O 180°) conformers, and not the expected *cis* and *gauche* forms[2] led to numerous investigations to determine the interactions responsible for this phenomenum. The F–C–C=O group has been shown to have a predominantly two-fold potential in fluoroacetic acid,[3] fluoroacetyl chloride[4] and fluoroacetone,[5,6] in all of which the equilibrium was shown to be between *cis* and *trans* forms. This contrasts with the situation in the analogous chlorine, bromine and iodine compounds in which the conformer equilibrium is, as expected, between the *cis* and *gauche* forms. In the difluorocompounds the situation is not so clear cut and both *cis–trans* and *cis–gauche* equilibria have been reported[6–8] (see ref. 6 for a detailed review).

In a recent paper in this series[6] a combined NMR/solvation and theoretical investigation examined the conformational isomerism in fluoroacetone (FA) and 1,1-difluoroacetone (DFA) using the solvent dependence of the $^4J_{HF}$, $^1J_{CF}$ and $^2J_{CF}$ couplings as experimental data. It was found that for FA the NMR data were in complete agreement with *ab initio* calculations at the MP2/6-31G* level. The conformational equilibrium was between the *cis* and *trans* conformers with the energy difference ($E_{cis} - E_{trans}$) varying from 2.2 kcal mol^{-1} in the vapour to −1.3 kcal mol^{-1} in DMSO solution. The extrapolated vapour state energy difference compared well with the calculated value of 2.8 kcal mol^{-1}. In 1,1-difluoroacetone (DFA) in contrast although the NMR data were consistent with the theoretical predictions that the *cis* (H–C–C=O 0°) conformer was the more stable vapour form, the experimental data showed clearly the presence of a second conformer which could only be derived from the theoretical calculations at the above level when solvent interactions were explicitly included in the iteration. This gave a minimum at a *gauche* conformer with (H–C–C=O *ca.* 104°). Again the energy difference ($E_{cis} - E_{trans}$) changed sign depending on the solvent, varying from 0.8 kcal mol^{-1} in the vapour to −1.2 kcal mol^{-1} in DMSO solution.

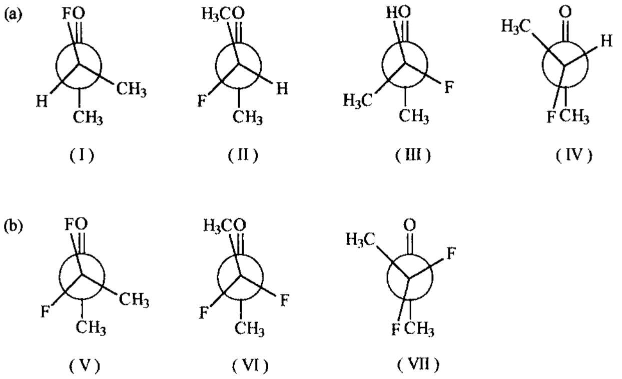

Fig. 1 Possible conformers for (a) 3-fluorobutan-2-one and (b) 3,3-difluorobutan-2-one.

Here we investigate the conformational equilibria in the related compounds 3-fluorobutan-2-one (FB) and 3,3-difluorobutan-2-one (DFB) in which a hydrogen has been replaced by a methyl group.

Shapiro and co-workers[9] examined the solvent dependence of the ^{1}H NMR spectra of FB, and discussed their results in terms of three possible conformers (I), (II) and (III) (Fig. 1) with the fluorine (I), methyl (II) and proton (III) eclipsing the carbonyl group. As the 4-methyl protons showed minimal solvent shifts in non-aromatic solvents, they ruled out conformation (II) in favour of the other two. Of these, the one with the eclipsed fluorine (I) is the more polar and should be stabilized

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† For Part 31, see ref. 1.

in polar solvents. The conformer (IV) where the fluorine is *trans* with the carbonyl group was not considered by Shapiro.

Here we extend Shapiro's NMR studies by recording the ^{1}H and ^{13}C spectra of FB and show that the $^4J_{HF}$, $^1J_{CF}$ and $^2J_{CF}$ couplings are sensitive to the F–C–C=O orientation. The use of *ab initio* plus solvation calculations allows us to define both the interconverting conformers in FB and also to obtain the conformer energy differences.

The ^{1}H and ^{13}C NMR spectra in different solvents for the 3,3-difluorobutan-2-one (DFB) are reported here for the first time as well as the *ab initio* calculations.

Theoretical

The *ab initio* calculations were performed using the GAUSSIAN94 program[10] and the solvation calculations using the MODELS program.[11] In the latter, the solvation energy of a molecule is given by including both the dipole and quadrupole reaction fields and also a direct dipole–dipole term to take account of the breakdown of the Onsager reaction-field theory in very polar media.

On this basis the solvation energy of any molecule in state A, *i.e.* the difference between the energy in vapour (E_A^V) and in any solvent (E_A^S) of relative permittivity ε is given by eqn. (1), where

$$E_A^V - E_A^S = k_A x/(1 - lx) + 3h_A x/(5 - x) + bf[1 - \exp(-bf/16RT)] \quad (1)$$

$x = (\varepsilon - 1)/(2\varepsilon + 1)$; $l = 2(n_D^2 - 1)/(n_D^2 + 2)$; $b = 4.30(a^{3/2}/r^3)(k_A + 0.5h_A)^{1/2}$ and $f = [(\varepsilon - 2)/(\varepsilon + 1)/\varepsilon]^{1/2}$ for $\varepsilon > 2$ and is zero otherwise, n_D is the refractive index, T is the temperature (K), k_A and h_A are μ_A^2/a^3 and q_A^2/a^5, μ_A and q_A being the dipole and quadrupole moments of molecule A and a is the solute radius, r is the solute–solvent distance and is taken as $a + 1.8$ Å. The solute radius is obtained directly from the molar volume (V_M) of the solute by the equation $V_M/N = 4\pi a^3/3$ where N is Avogadro's number. The molar volume can be obtained from the density of pure liquid, if known, or directly in the program from additive atomic volumes. Similarly the solute refractive index may be inserted if known or can be calculated directly from additive contributions.

For a molecule in state B a similar equation is obtained differing only in the values of k_B and h_B. Subtraction of the two equations gives the experimentally required quantity ΔE^S ($E_A^S - E_B^S$), the energy difference in any solvent S of given relative permittivity, in terms of ΔE^V ($E_A^V - E_B^V$) and calculable or measurable parameters. This theory has been given in detail previously and was shown to give an accurate account of the solvent dependences of a variety of conformational equilibria.[11–13]

In the early applications of this theory the dipole and quadrupole moments of the molecules (μ and q) were calculated by placing point dipoles along the appropriate bonds. This has now been replaced by the more accurate and computationally simpler procedure of calculating these parameters directly from the partial atomic charges in the molecule, calculated from the CHARGE routine.[14]

An important factor in the determination of the conformational equilibrium between two conformers of very different dipole moments is that the temperature dependence of pure liquid (or solvent) relative permittivity (previously known as dielectric constant) can appreciably affect the value of the energy difference obtained. It has been shown[11] that the true value of the free energy difference at any temperature [$\Delta H(t)$] is related to that obtained using the Van't Hoff eqn. (2), by eqn. (3).

$$\mathrm{d}\ln K/\mathrm{d}(1/t) = -\Delta H^\circ/R \quad (2)$$

$$\Delta H(t) = \Delta H^\circ + T(\mathrm{d}H/\mathrm{d}t) \quad (3)$$

Table 1 Calculated geometries for 3-fluorobutan-2-one and 3,3-difluorobutan-2-one

Parameter	3-Fluorobutan-2-one *trans* Calc.[a]	3-Fluorobutan-2-one *cis* Calc.[a]	3,3-Difluorobutan-2-one *cis* Calc.[a]
r(C=O)	1.192	1.188	1.188
r(C–C)	1.523	1.524	1.534
$r(C–C_{Me})$	1.506	1.511	1.506
r(C–F)	1.375	1.362	1.351
$r(C_{Me}–H)$[b]	1.082	1.083	1.082
$r(C_F–H)$	1.084	1.086	—
∠C–C=O	118.54	120.94	119.81
∠Me–C=O	123.19	122.46	123.96
∠F–C–C	109.51	108.85	107.04
∠C–C–C	112.17	111.68	115.83
∠H–C_F–C	107.60	109.42	—
∠H–C_{Me}–C[b]	109.96	110.16	109.69
θ(F–C–C=O)	178.28	22.89	—
θ(C–C–C=O)	—	—	0.03
E[c]	−330.66092	−330.655053	−429.691670
$E_{rel.}$[d]	0.00	3.67	—
Dipole mom.[e]	1.30	4.30	0.70

[a] MP2/6-31G**. [b] Averaged values. [c] Hartrees. [d] kcal mol^{-1} (1 cal = 4.184 J). [e] D.

Table 2 Parameters for reaction-field calculations for 3-fluorobutan-2-one

Rotamer	Dipole moment/ D	k/kcal mol^{-1}	h/kcal mol^{-1}	n_D	V_M	l
trans	1.1	0.5071	6.5448	1.3672	91.110	0.4493
cis	4.4	7.9012	1.2986			

The correction factor $T(\mathrm{d}H/\mathrm{d}t)$ has been shown to be as much as 0.5 kcal mol^{-1} for moderately polar solutes and solvents,[6,11] thus it cannot be ignored in any accurate determination of conformer energies.

3-Fluorobutan-2-one

To our knowledge there has been no previous theoretical study of the conformations of this molecule. Its geometry was optimized at the MP2/6-31G** level with zero point energy correction (ZPE),[15] and two stable conformers were found, the *cis* and *trans*. Their geometries and relative energy are given in Table 1. The *trans* rotamer [(IV), Fig. 1] had not been considered a stable rotamer by Shapiro,[9] but we found that it is the most stable rotamer. The *ab initio* dipole moments are 1.30 D (*trans*) and 4.30 D (*cis*). Using the *ab initio* geometries, the CHARGE routine gave dipole moments which compare very well (*trans* 1.15 D and *cis* 4.28 D) to those from *ab initio*. Thus, the CHARGE partial atomic charges may be used with confidence in the MODELS solvation calculations. The parameters required to calculate the solvation energy through eqn. (1) are given in Table 2. The refractive index and molar volume were calculated by the program.

3,3-Difluorobutan-2-one

There has also been no previous theoretical study of this molecule. When the molecular geometry was optimized at the MP2/6-31G** level with the ZPE correction, only one stable conformer, the *cis* (C–C–C=O 0°), was found. The *trans* form is at a maximum in the potential surface (Fig. 2), and increasing the size of basis set to MP2/6-311G** gave the same results.

Experimental

The solvents were obtained commercially, stored over molecular sieves and used without further purification.

Table 3 Chemical shifts (ppm) and coupling constants (Hz) for 3-fluorobutan-2-one

Solvent	ε	H^1	H^3	H^4	C^1	C^2	C^3	C^4	$^3J_{HH}$	$^2J_{HF}$	$^3J_{HF}$	$^4J_{HF}$	$^1J_{CF}$	$^2J_{CF}{}^a$	$^2J_{CF}{}^b$
CCl_4–C_6D_{12}	2.24	2.20	4.72	1.43	24.55	206.29	92.33	17.18	7.00	46.45	23.46	4.92	181.7	26.1	22.3
$CDCl_3$	4.81	2.26	4.85	1.46	25.19	208.77	92.81	17.42	6.69	49.62	23.84	4.63	181.5	25.3	22.3
CD_2Cl_2	8.93	2.21	4.85	1.43	25.36	208.54	93.26	17.59	6.95	49.52	23.98	4.45	180.8	24.6	22.3
Pure liq.	12.73	2.17	4.87	1.40	25.01	208.14	93.45	17.43	6.92	49.42	23.88	4.42	179.8	24.4	22.3
Acetone-d$_6$	20.70	2.19	4.95	1.43	25.19	207.95	93.38	17.47	6.89	49.24	23.84	4.21	179.4	24.0	22.5
CD_3NO_2	35.90	2.17	4.93	1.43	25.56	208.74	93.66	17.63	6.91	49.18	24.08	4.02	179.1	23.0	22.3
CD_3CN	37.50	2.18	4.94	1.44	25.37	209.77	94.16	17.66	6.97	49.21	24.28	3.96	179.1	22.8	22.3
DMSO-d$_6$	46.70	2.17	5.05	1.39	25.24	207.49	92.25	16.96	6.92	48.84	24.13	3.86	178.7	22.5	22.1

[a] $^2J_{CF}$ between F–C–C=O. [b] $^2J_{CF}$ between H_3C–C–F.

Table 4 Temperature dependence of HF couplings (Hz) for 3-fluorobutan-2-one in $FCCl_3$, acetone-d$_6$ and DMSO-d$_6$

$FCCl_3$					Acetone-d$_6$					DMSO-d$_6$				
Temp./K	$^3J_{HH}$	$^2J_{HF}$	$^3J_{HF}$	$^4J_{HF}$	Temp./K	$^3J_{HH}$	$^2J_{HF}$	$^3J_{HF}$	$^4J_{HF}$	Temp./K	$^3J_{HH}$	$^2J_{HF}$	$^3J_{HF}$	$^4J_{HF}$
293	6.87	49.90	23.49	4.98	293	6.91	49.27	23.92	4.25	293	6.95	48.79	24.17	3.85
273	6.92	49.89	23.48	5.08	273	6.98	49.19	23.91	4.32	313	6.93	48.85	24.10	3.79
253	6.92	49.89	23.49	5.20	253	6.91	49.20	23.90	4.33	333	6.92	48.92	24.10	3.79
233	6.92	49.89	23.59	5.30	233	6.91	49.11	23.91	4.40	353	6.86	48.92	24.04	3.72
					193	6.98	49.04	23.99	4.56	373	6.80	48.98	24.04	3.72

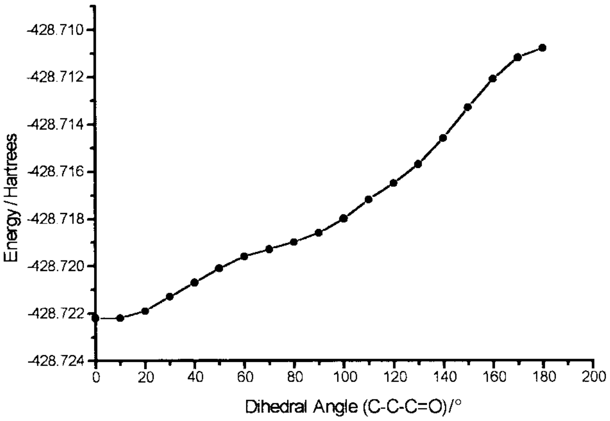

Fig. 2 Potential energy surface for 3,3-difluorobutan-2-one at the MP2/6-31G** level.

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AMX 400 spectrometer operating at 400.14 MHz for proton and 100.63 MHz for carbon, and on a Varian Gemini 300 operating at 300.06 MHz for proton and 75.45 MHz for carbon. Spectra were of *ca.* 20 mg cm^{-3} solutions with a probe temperature of *ca.* 25 °C. [$^2H_{12}$]Cyclohexane was used as the deuterium lock signal for the CCl_4 solution and pure liquid and [$^2H_6$]benzene external lock was used for $CFCl_3$ solution. The ^{1}H and ^{13}C spectra were all referenced to Me_4Si. Typical conditions were: proton spectra 48 transients, spectral width 3000 Hz with 32 K data points and zero filled to 128 K to give a digital resolution of 0.04 Hz. Proton-decoupled carbon spectra were obtained with typical conditions 528 transients, 3 s pulse delay, spectral width 22000 Hz with 64 K data points and zero filled to 256 K for a 0.1 Hz digital resolution.

The spectra were all first-order and the coupling constants and chemical shifts taken directly from the spectra. The temperature dependence of the proton spectrum of FB was recorded in non-polar and polar solvents. The NMR data are presented in Tables 3, 4 and 5.

The IR spectra were recorded with a Bomem model MB 100 FTIR spectrometer, using a sodium chloride cell with 0.5 mm spacer for dilute (*ca.* 0.05 M) solutions, with the solvent as background when recording the solute spectrum.

3-Fluorobutan-2-one. The synthesis was carried out in a 250 mL three-neck flask, equipped with addition funnel, magnetic stirrer, a distillation head and condenser to remove the FB immediately after its formation. 3-Chlorobutan-2-one (21.1 g, 0.198 mol) was reacted with potassium bifluoride (41.0 g, 0.515 mol) in 150 mL of dry diethylene glycol at 160 °C. The low-boiling product immediately distilled over. The NMR spectrum of the distillate showed the correct pattern for FB and also indicated the presence of some 3-chlorobutan-2-one. Redistillation gave pure FB, bp 70–72 °C (lit.[9] bp 74–76 °C). 8.4 g (47% yield) were obtained.

3,3-Dichlorobutan-2-one. Butan-2-one (29 g, 0.402 mol) was placed in a 125 mL three-neck flask equipped with a condenser, addition funnel and magnetic stirrer. Sulfuryl chloride (108.5 g, 0.804 mol) was added dropwise over a period of 90 min. The reaction was very exothermic and the temperature was maintained between 40 and 50 °C by controlling the rate of addition. The reaction was kept under stirring overnight. The reaction mixture was washed with water (3 × 30 mL) and with a 10% sodium hydrogen carbonate solution (3 × 30 mL) and again with water. The compound was distilled through a Vigreux column, resulting in three fractions, the first one 4.2 g of the 1,1-dichlorobutan-2-one, bp 102 °C; the second 11.5 g of the 3,3-dichlorobutan-2-one, bp 120 °C and the last one 11.0 g of the 1,3-dichlorobutan-2-one, bp 160 °C.[11] The ^{1}H NMR spectrum in $CDCl_3$ for 3,3-dichlorobutan-2-one showed two singlets at 2.55 ppm and 2.17 ppm.

3,3-Difluorobutan-2-one. In a 250 mL three-neck flask, equipped with magnetic stirrer and reflux condenser. Potassium bifluoride (52 g, 0.664 mol) in dry diethylene glycol was added, followed by the addition of 3,3-dichlorobutan-2-one (31 g, 0.221 mol). The reaction mixture was heated up to 190 °C over a period of 7 hours.[16]

Steam distillation of the reaction products gave 25 mL of a water–3,3-difluorobutan-2-one mixture. Redistillation gave pure 3,3-difluorobutan-2-one, bp 50 °C (lit.[17] 49 °C), 1.2 g (5% yield) were obtained.

Results

The NMR data of Tables 3, 4 and 5 can now be used with the results of the theoretical calculations given earlier to determine the conformational equilibrium in these molecules.

Table 5 Chemical shifts (ppm) and coupling constants (Hz) for 3,3-difluorobutan-2-one

Solvent	ε	H^1	H^2	C^1	C^2	C^3	C^4	$^3J_{HF}$	$^4J_{HF}$	$^1J_{CF}$	$^2J_{CF}{}^a$	$^2J_{CF}{}^b$
CCl_4–C_6D_{12}	2.24	2.29	1.66	22.37	196.50	117.25	18.50	18.97	1.55	249.2	33.7	24.9
$CDCl_3$	4.81	2.33	1.68	23.23	198.81	117.70	18.99	19.18	1.61	249.0	33.3	25.1
CD_2Cl_2	8.93	2.31	1.68	23.61	199.16	118.27	19.37	19.32	1.65	248.9	32.7	25.0
Acetone-d_6	20.70	2.32	1.69	23.63	199.53	119.07	19.49	19.47	1.63	248.6	32.0	25.2
CD_3CN	37.50	2.30	1.68	24.08	200.12	119.21	19.77	19.65	1.66	247.8	31.8	25.1
DMSO	46.70	2.33	1.72	23.74	199.10	118.11	19.18	19.87	1.64	248.6	31.2	24.9
Pure liq.		2.88	2.25	22.66	198.88	118.44	18.68	19.33	1.50	248.1	32.8	25.4

[a] $^2J_{CF}$ between F–C–C=O. [b] $^2J_{CF}$ between H_3C–C–F.

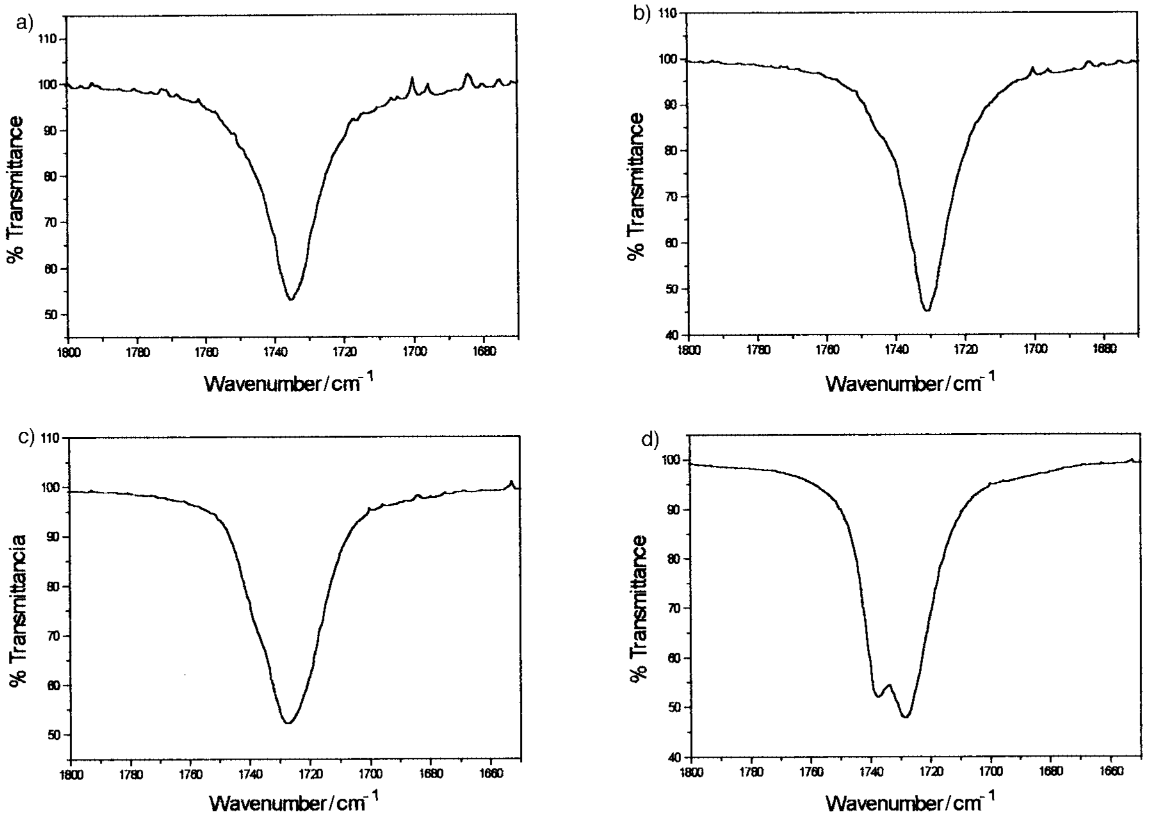

Fig. 3 The carbonyl absorption band in the IR spectrum of FB in a) hexane, b) CCl_4, c) $CHCl_3$ and d) CH_3CN.

Although the use of $^3J_{HH}$ couplings in conformational investigations is well established,[13] this is not the case for the HF and CF couplings measured here. Thus, it is first necessary to determine how much of the observed variation of the couplings is due to changes in the conformer populations and how much to an intrinsic solvent dependence.

This question had been answered for the fluoroacetone (FA) and 1,1-difluoroacetone[6] by comparing the changes in coupling constants in FA and DFA with those of 1,1,1-trifluoroacetone (TFA) in which there is only one possible conformer. However, for the 3-fluorobutan-2-one a similar comparison is not possible. An alternative method of isolating the changes in the couplings due to population changes is simply to plot one variable against another. If the changes are solely due to population changes, the plots are linear.[6] This procedure showed that for FB, the $^4J_{HF}$ *vs.* $^2J_{CF}$ plot is accurately linear (corr. coeff. 0.995), but this is not the case for $^1J_{CF}$ *vs.* $^4J_{HF}$ and *vs.* $^2J_{CF}$ (corr. coeffs. 0.955 and 0.950 respectively). Thus, we will consider initially only the $^4J_{HF}$ and $^2J_{CF}$ couplings.

3-Fluorobutan-2-one

The NMR data in Table 3 may be combined with the solvation calculations given earlier to provide a detailed account of the conformational equilibrium in this compound, which may be described in terms of the *cis* and *trans* conformers [eqn. (4)].

$$\begin{aligned} J_{obs} &= n_{cis}J_{cis} + n_{trans}J_{trans} \\ n_{cis} + n_{trans} &= 1 \\ n_{cis}/n_{trans} &= \exp(-\Delta E/RT) \\ \Delta E &= E_{cis} - E_{trans} \end{aligned} \tag{4}$$

The value of $^4J_{HF}$ in pure liquid (4.42 Hz) gives, with the data of Table 3, an interpolated value of 12.7 for the pure liquid relative permittivity.

The variable temperature NMR data (Table 4) show that the $^4J_{HF}$ coupling decreases with increasing temperature in $FCCl_3$ (5.30→4.98 Hz), acetone-d_6 (4.56→4.25 Hz) and DMSO-d_6 (3.85→3.72) solutions. These results indicate that one of the rotamers predominates over the other in all solvents used in this study. The IR spectra of FB in different solvents (Fig. 3) correlate with the NMR data, showing either a shoulder (in CCl_4 and $CHCl_3$) or two partially resolved (in CH_3CN) carbonyl bands, the one at lower wavenumber being the more intense one, which can be ascribed to the less polar *trans* conformer as has already been observed for similar α-heterosubstituted carbonyl compounds.[18]

With these considerations the solvent data in Table 3 may be used with the solvation theory to search for the best solution

Table 6 Conformer energy difference (kcal mol^{-1}) and observed and calculated couplings for 3-fluorobutan-2-one

Solvent	ε	$E_{cis} - E_{trans}$ [a]	$^4J_{HF}$ Calc.	$^4J_{HF}$ Obs.
CCl_4–C_6D_{12}	2.24	2.57	5.03	4.92
$CDCl_3$	4.81	1.69	4.90	4.63
CD_2Cl_2	8.93	1.18	4.69	4.45
Pure liquid	12.73	0.94	4.53	4.42
Acetone-d_6	20.70	0.65	4.28	4.21
CD_3NO_2	35.90	0.32	3.90	4.02
CD_3CN	37.50	0.29	3.86	3.96
DMSO-d_6	46.70	0.14	3.67	3.86

[a] $\Delta E^V = 3.7$ kcal mol^{-1}.

for both the conformer energy difference and the values of J_{cis} and J_{trans}.

This gave values of ΔE^V of 3.7 kcal mol^{-1}, J_{cis} 1.89 Hz and J_{trans} 5.06 Hz, and the solution energy differences and couplings of Table 6. The values of the remaining couplings in the two conformers may be obtained directly from the previously noted linear relationships between the couplings in Table 3. This gives for the $^1J_{CF}$ and $^2J_{CF}$ couplings in the *cis* rotamer 172.6 Hz and 15.6 Hz and for the *trans* rotamer 182.3 Hz and 26.7 Hz, respectively.

3,3-Difluorobutan-2-one

The NMR data in Table 5 can now be combined with the *ab initio* calculations to determine the conformational isomerism in this compound.

The GAUSSIAN calculations show clearly the presence of only one conformer. Table 5 shows that the coupling constants do not change with solvent. The FTIR spectrum of DFB was also recorded in solvents of varying polarity. In all solvents the carbonyl absorbtion is a single sharp band, confirming that the NMR data is in agreement with *ab initio* calculations and that there is only one stable conformer (*cis* C–C–C=O 0°) for DFB both in the vapour phase and in solution.

Discussion

The NMR and IR experimental data combined with the solvation calculations provide a consistent analysis of the conformational isomerism in the molecules studied here.

In FB the equilibrium is between the *cis* and *trans* rotamers as predicted by theory. The energy difference ($E_{cis} - E_{trans}$) is 3.7 kcal mol^{-1} in the vapour phase, which compares very well with that calculated by GAUSSIAN94 (3.6 kcal mol^{-1}).

A small change in structure (the replacement of a hydrogen atom by a methyl group) shifts the conformational equilibrium significantly. In fluoroacetone (FA)[6] the *trans* rotamer predominates over the *cis* only in solvents of low polarity (CCl_4, CS_2 and $CDCl_3$), while for 3-fluorobutan-2-one the *trans* rotamer predominates over the *cis* in all solvents (CCl_4 to DMSO-d_6).

The NMR and IR data, and *ab initio* calculations are consistent in showing clearly the presence of only one stable conformer (*cis* C–C–C=O 0°) for 3,3-difluorobutan-2-one (DFB). This differs from that of 1,1-difluoroacetone (DFA)[6] in that DFA exists as two stable conformers *cis* and *gauche* both in the vapour phase and in solution. Both these effects are presumably due to the increased steric repulsion between the two methyl groups in the *gauche* conformer (V, Fig. 1) of DFB (*cf.* 0.9 kcal mol^{-1} repulsion in *gauche* butane) which destabilizes the *cis* conformer in FB and removes the *gauche* minimum in the potential energy curve of DFA.

The coupling constants obtained for the individual conformers of FB and DFB may be compared with those obtained similarly for FA and DFA.[6] In ref. 6 the $^4J_{HF}$ conformer couplings were observed to be proportional to $\cos^2\theta$ where (θ = F–C–C–CH_3 dihedral angle). Combining the two sets of data and making allowances for any errors in the extrapolated couplings gives eqn. (5) which may be of use in any future investigation involving this molecular fragment.

$$\begin{aligned} ^4J_{HF}\ (\text{F–C–CO–CH}_3) &= 5.1\cos^2\theta - 0.1\ (0° < \theta < 90°) \\ &= 3.1\cos^2\theta - 0.1\ (90° < \theta < 180°) \quad (5) \end{aligned}$$

The extrapolated values of the $^2J_{CF}$ couplings in the *cis* and *trans* conformers of FB are *ca.* 16 and 26.5 Hz respectively and these also compare very well with the analogous values in FA (16.2 and 23.5 Hz).[6] These cannot be combined with the $^2J_{CF}$ couplings in the difluoro compounds as the influence of the geminal fluorine atom on this coupling is too large to be ignored. This factor is even more noticeable in the $^1J_{CF}$ couplings which differ greatly in the mono and difluoro compounds.

Acknowledgements

We acknowledge CNPq for a scholarship-SWE (C. F. T.) and fellowship (R. R.), and CENAPAD-SP for the the computer facilities (GAUSSIAN94). Financial support from FAPESP and Dr P. Leonard's assistance in using the Bruker AMX 400 spectrometer are gratefully acknowledged.

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