Stereodynamics of 4-substituted cyclohexenes. Formyl, vinyl and methyl substituents. Dynamic NMR and molecular mechanics studies

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ABSTRACT: The ^{1}H and ^{13}C{^{1}H} NMR spectra of 4-formylcyclohexene in 50% CF_2Cl_2–50% CHF_2Cl decoalesce at very low temperatures and, at 108 K, have sharpened into a major (77%) and a minor (23%) subspectrum. Based on the NMR spectra and molecular mechanics calculations, the major subspectrum is assigned to a family of equatorial conformations and the minor subspectrum to a family of axial conformations. The free energy of activation for conversion of the equatorial conformations to the axial forms is 5.6 kcal mol^{-1} (1 kcal = 4.184 kJ) at 117 K. Within a family of conformations, interconversion occurs rapidly at 108 K via formyl group rotation. The conformational preference in 4-formylcyclohexene is solvent dependent. In 50% CF_2Cl_2–50% CHF_2Cl, CHF_2Cl and CF_2Cl_2, the respective ratios of equatorial to axial conformations are 77:23, 77:23, and 89:11 at 108 K. The ^{1}H and ^{13}C{^{1}H} NMR spectra of 4-methylcyclohexene and 4-vinylcyclohexene in 50% CF_2Cl_2–50% CHF_2Cl show no evidence of decoalescence at very low temperatures but do show differential broadening and subsequent sharpening of various resonances characteristic of exchange between strongly dominant equatorial conformations and axial conformations present at too low a concentration to be detectable by NMR. A lower limit on the free energy preference for the equatorial conformations is estimated to be 1.0 kcal mol^{-1}. Molecular mechanics calculations also predict a stronger preference for equatorial conformations in 4-methylcyclohexene and 4-vinylcyclohexene than in 4-formylcyclohexene. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: 4-formyl-, methyl- and -vinylcyclohexene; stereodynamics; conformation; dynamic NMR; molecular mechanics

INTRODUCTION

The cyclohexene ring is prevalent in organic chemistry. Assessing the stereodynamics of cyclohexene and substituted cyclohexenes is important in developing a comprehensive understanding of the chemistry of derivatives of this important ring system.[1] Cyclohexene exists as two enantiomeric half-chair conformations (C_2 symmetry). Dynamic NMR (DNMR) studies established a free energy of activation ($\Delta G^{\ddagger}$) of 5.3–5.4 kcal mol^{-1} (1 kcal = 4.184 kJ) for the enantiomerization.[2] Based on numerous molecular mechanics calculations[1b] and recent *ab initio* calculations,[3] the boat conformation (C_s symmetry) is consistently predicted to be the transition state for conformational exchange in cyclohexene. The *ab initio* calculations predict a barrier for enantiomerization of 5.5 kcal mol^{-1}, in excellent agreement with the DNMR results. Substituent effects on the ring inversion

barrier are consistent with the boat being the transition state.[2b,4]

Direct measurements of the distribution between axial and equatorial conformations in a large number of monosubstituted cyclohexanes have been made by examination of the NMR spectra at low temperature under conditions of slow exchange on the NMR chemical exchange time-scale.[5] In contrast, the axial versus equatorial conformational preferences have been measured directly by NMR at low temperature for only seven substituents in 4-substituted cyclohexenes (F, Cl, Br, I, OH, OSiMe$_3$, CN).[2b,6,7] As predicted in an early report,[2b] the conformational preferences of polar 4-substituents are solvent dependent. Cyclohexene has a dipole moment of 0.75 D with the moment coincident with the C_2 symmetry axis.[8] With a polar substituent at the 4-position, the net dipole moment of the axial conformation will be greater than that of the equatorial form; the axial conformer should be more favored in solvents of higher polarity.[2b] Solvents of lower polarity will stabilize the equatorial conformation. For example, the free energy difference between the axial and equatorial conformations (axial $\rightleftharpoons$ equatorial) of 4-chlorocyclohexene is -0.31 kcal mol^{-1}

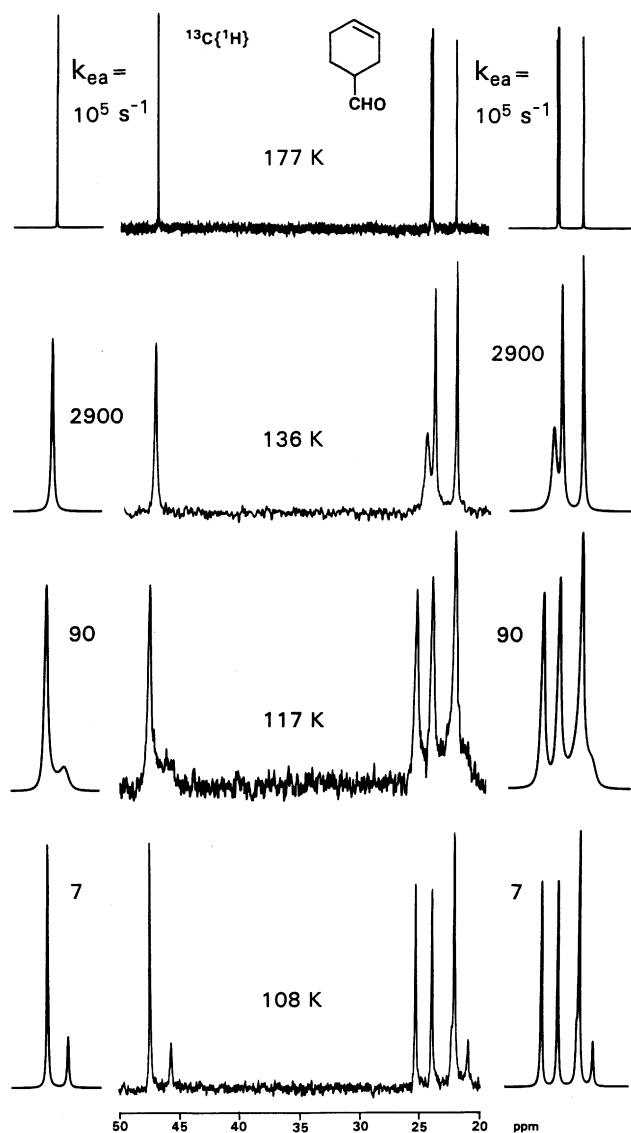**Correspondence to:* C. H. Bushweller, Department of Chemistry, University of Vermont, Burlington, Vermont 05405-0125, USA.

Figure 1. Experimental $^{13}C\{^{1}H\}$ DNMR spectra (125.76 MHz) of the aliphatic carbons of 4-formylcyclohexene (10% v/v in 50% CF_2Cl_2–50% CHF_2Cl) in the middle column and theoretical simulations at the right and left. The rate constant (k_{ea}) is associated with the conversion of equatorial to axial conformations

at 128 K in the non-polar CF_2Cl_2, -0.20 kcal mol^{-1} at 113 K in CD_2CDCl and $+0.02$ kcal mol^{-1} at 128 K in the polar CHF_2Cl (axial conformation slightly favored).

The conformational preferences in just one 4-substituted-cyclohexene in which the substituent (cyano) has carbon bonded to C-4 has been measured directly by NMR spectroscopy under slow-exchange conditions.[7] This paper reports $^{13}C\{^{1}H\}$ and ^{1}H DNMR studies of 4-formylcyclohexene in solvents of different polarity allowing the direct determination of axial versus equatorial conformational partitioning and the barrier to conformational interconversion. Molecular mechanics calculations using the MMX force field are in good agreement with the NMR data in CF_2Cl_2 and suggest that

each of the axial and equatorial conformations exists as a family of two diastereomeric forms that interconvert rapidly via formyl group rotation even at very low temperatures.[9] Indirect DNMR evidence allows a lower limit of 1.0 kcal mol^{-1} to be placed on the free energy preference for the equatorial conformations over the axial forms in 4-vinylcyclohexene and 4-methylcyclohexene.

RESULTS AND DISCUSSION

4-Formylcyclohexene

The $^{13}C\{^{1}H\}$ NMR spectrum (125.76 MHz) of 4-formylcyclohexene (10% v/v in 50% CF_2Cl_2–50% CHF_2Cl) at 177 K shows aliphatic carbon resonances at 22.5, 24.6, 24.7 and 47.3 ppm, olefinic carbon signals at 125.9 and 128.2 ppm and the carbonyl carbon resonance at 206.4 ppm. Triplets for each of the two solvents are observed at 117.6 ppm (CHF_2Cl; $^{1}J_{CF} = 290$ Hz) and 127.1 ppm (CF_2Cl_2; $^{1}J_{CF} = 320$ Hz). The aliphatic carbon resonances are illustrated in Figure 1. Below 140 K, each of the aliphatic carbon resonances decoalesces (Figure 1) whereas the olefinic and carbonyl resonances do not show any clear decoalescence. A sharpened spectrum is observed at 108 K (Figure 1). At 108 K, C-4 shows a dominant resonance at 47.5 ppm (77%) and a minor signal at 45.8 ppm (23%). As determined from complete lineshape simulations, the other three aliphatic carbon resonances show exactly analogous decoalescence behavior.[10] For each aliphatic carbon, the chemical shifts of the dominant resonance and its minor chemical exchange partner are listed in Table 1. A decomposition of the theoretical simulation at 108 K is illustrated in Figure 2. Resonances due to the major species are shown in the top subspectrum of Figure 2 with the minor subspectrum second from the top. Exchange partners are labeled with asterisks, open circles, solid circles and boxes. The composite spectrum with $k_{ea} = 0$ s^{-1} in Figure 2 results from superposition of the two properly weighted subspectra. The bottom composite subspectrum incorporates a rate of chemical exchange necessary to achieve an accurate fit at 108 K. Simulations of the $^{13}C\{^{1}H\}$ DNMR spectra at other temperatures are illustrated in Figure 1.

Table 1. ^{13}C NMR chemical shifts of the pairs of major and minor chemical exchange resonances for the aliphatic carbons of 4-formylcyclohexene[a]

Major resonance (ppm)	Minor chemical exchange partner (ppm)
47.48	45.75
25.60	22.65
24.23	22.45
22.45	21.29

[a] At 108 K.

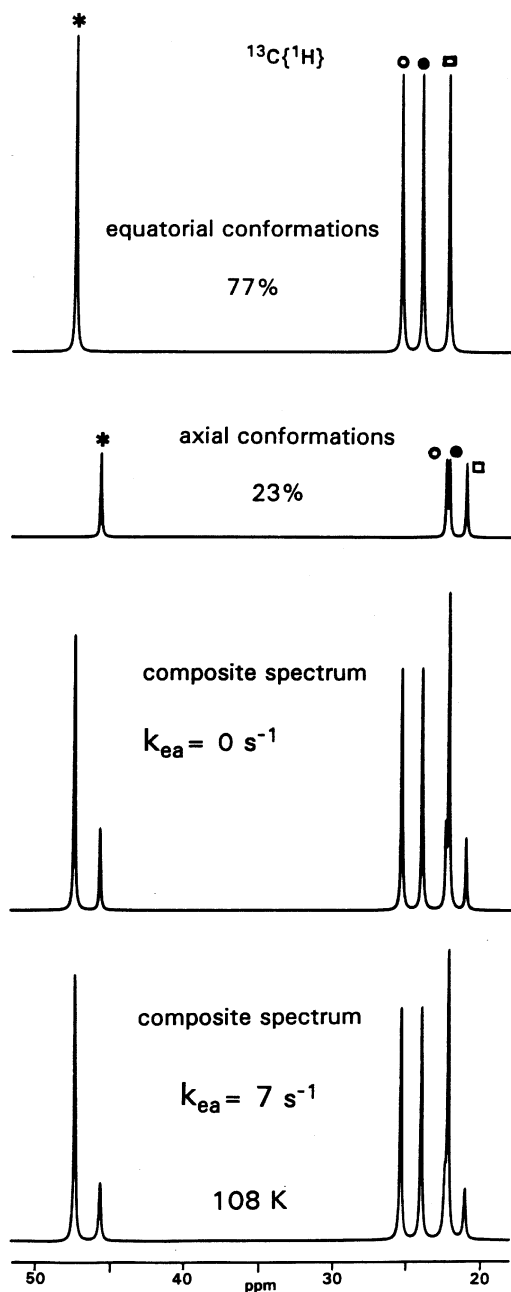**Figure 2.** Decomposition of the theoretical simulation of the $^{13}C\{^1H\}$ NMR spectrum of the aliphatic carbons of 4-formylcyclohexene at 108 K

The free energy of activation for conversion of the major to the minor species is 5.6 kcal mol^{-1} at 117 K.

The $^{13}C\{^1H\}$ NMR spectrum of 4-formylcyclohexene at 108 K shows the presence of major and minor equilibrium conformations but does not allow unequivocal assignments of conformation. Assignments can be made by examination of the ^1H DNMR spectra.

The ^1H NMR spectrum (500.16 MHz) of 4-formyl-cyclohexene (10% v/v in 50% CF_2Cl_2–50% CHF_2Cl) at 200 K shows a slightly broadened singlet ($\Delta\nu_{1/2} = 1.8$ Hz) at 9.68 ppm (1H; CHO), a multiplet at 5.69–
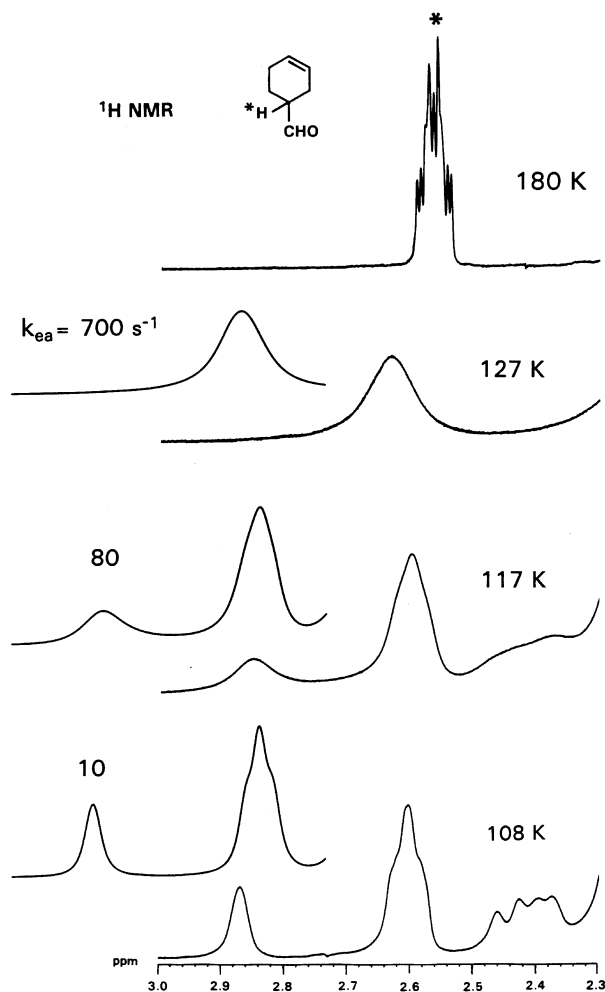

Figure 3. Experimental ^1H DNMR spectra (500.16 MHz) of the C-4 proton of 4-formylcyclohexene (10% v/v in 50% CF_2Cl_2–50% CHF_2Cl) and theoretical simulations offset to the upper left. The rate constant (k_{ea}) is associated with the conversion of equatorial to axial conformations

5.75 ppm (2H; HC=CH) and a multiplet at 2.53–2.60 ppm (1H; C-4 proton), with other multiplets at 2.17–2.27 ppm (2H), 2.04–2.17 ppm (3H) and 1.58–1.68 (1H) for the remaining aliphatic protons. At temperatures below 130 K, all resonances, except the aldehydic proton resonance, decoalesce. The decoalescence of the C-4 proton signal is salient and is illustrated in Figure 3. At 108 K, a resharpened spectrum shows a minor, relatively narrow C-4 proton signal at 2.87 ppm and a major C-4 proton signal at 2.61 ppm that is significantly broader and shows partially resolved fine structure. The ratio of the integrated intensities of the peak at 2.61 ppm to that at 2.87 ppm is 3.5:1.0 at 108 K. Based on a well established rationale, the narrow resonance at 2.87 ppm is assigned to the equatorial C-4 proton on the axial conformation.[2b] The broader signal at 2.61 ppm is assigned to the axial C-4 proton on the equatorial conformer. The distribution of axial (22%) and equatorial (78%) conformations at 108 K

determined by ^{1}H NMR is in excellent agreement with the ^{13}C NMR data (23% and 77%), allowing assignment of the major and minor subspectra observed in the ^{13}C NMR spectra.

A rigorous theoretical simulation of the DNMR behavior of the C-4 proton resonance requires exchange between two six-spin systems, each of which has six unique chemical shifts. This problem is beyond the capability of current DNMR lineshape programs. Based on the narrow aldehydic proton resonance (see above), it is apparent that spin–spin coupling of the aldehydic proton to the C-4 proton is very small (<2 Hz). By ignoring this coupling and by using a simplified five-spin, two-conformation chemical exchange model that employed the symmetry pairing option in computer program DNMR6, acceptable simulations were achieved (Figure 3).[10] Acceptable simulation of the resonance at 2.61 ppm required the use of two $^3J_{HCCH}$ values of about 11 Hz, one of about 2 Hz and another about 5 Hz. The large $^3J_{HCCH}$ values are consistent with vicinal protons that are *anti* to each other and consistent with assignment of the signal at 2.61 ppm to the C-4 axial proton on the equatorial conformation of 4-formylcyclohexene. In this conformation, the C-4 axial proton is also *gauche* to two vicinal equatorial protons that will show smaller $^3J_{HCCH}$ coupling to the C-4 proton. The signal at 2.87 ppm is simulated using all $^3J_{HCCH}$ values that are less than 4 Hz consistent with all four vicinal protons being *gauche* to the C-4 proton; this resonance is assigned to the equatorial proton on the axial conformation of 4-formylcyclohexene. From the ^{1}H DNMR simulation at 117 K (Figure 3), the free energy of activation for equatorial to axial conversion is 5.6 kcal mol^{-1}, also in agreement with the 13C DNMR value (5.6 kcal mol^{-1}). Thus, 4-formylcyclohexene shows a slight free energy preference (0.26 kcal mol^{-1}) for the equatorial conformation in 50% CF$_2$Cl$_2$–50% CHF$_2$Cl at 108 K.

The conformational preference of 4-formylcyclohexene is solvent dependent. At 106 K in pure CHF$_2$Cl, the ^{13}C{^{1}H} NMR spectrum shows two C-4 signals at 47.7 and 46.0 ppm with a respective intensity ratio of 3.3:1.0; conformational preference is essentially identical with that in 50% CF$_2$Cl$_2$–50% CHF$_2$Cl. At 106 K in pure CHF$_2$Cl, the ^{1}H NMR spectrum shows an axial C-4 proton resonance (equatorial formyl) at 2.65 ppm and an equatorial C-4 proton signal (axial formyl) at 2.89 ppm also with a respective intensity ratio of 3.3:1.0. However, in pure CF$_2$Cl$_2$ at 106 K, the ^{13}C{^{1}H} NMR spectrum shows two C-4 signals at 47.0 and 44.7 ppm with a respective intensity ratio of 8.1:1.0, showing an increase in the percentage of the equatorial conformation from 77% in the polar CHF$_2$Cl to 89% in the non-polar CF$_2$Cl$_2$. Conformational preferences are compiled in Table 2. An analysis of time-averaged vicinal coupling constants in selectively deuterated 4-formylcyclohexene at room temperature in the polar CHCl$_3$ reveals 70% equatorial conformations ($\Delta G^\circ = -0.5$ kcal mol^{-1})[11] as compared

Table 2. Conformational preferences in 4-formylcyclohexene

Solvent	K_{eq} (ax $\rightleftharpoons$ eq)	ΔG° (kcal mol^{-1})
CF$_2$Cl$_2$	8.1	−0.44[a]
50% CF$_2$Cl$_2$–50% CHF$_2$Cl	3.3	−0.26[b]
CHF$_2$Cl	3.3	−0.26[a]

[a] At 106 K.
[b] At 108 K.

Table 3. MMX-calculated relative energies of equilibrium conformations of 4-formylcyclohexene

Conformation[a]	Energy (kcal mol^{-1})
1	0.0[b]
2	0.0
4	0.7
5	1.0

[a] See Scheme 1.
[b] $\Delta H_f = -28.9$ kcal mol^{-1}.

with our direct measurement in the polar CHF$_2$Cl at 106 K ($\Delta G^\circ = -0.26$ kcal mol^{-1}).

Molecular mechanics calculations for 4-formylcyclohexene using the MMX force field predict six equilibrium conformations, four of which will be present at concentrations high enough to be detectable by NMR (Table 3).[9] With the formyl group in the equatorial conformation, the MMX force field predicts three equilibrium conformations including isoenergetic conformations **1** ($\Delta H_f = -28.91$ kcal mol^{-1}) and **2** ($\Delta H_f = -28.87$ kcal mol^{-1}) shown in Scheme 1. In **1**, the C-3—C-4—C=O torsion
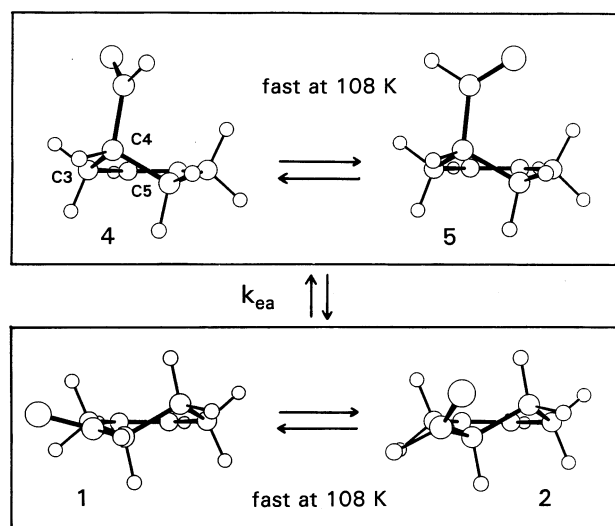
Scheme 1. Dominant equilibrium conformations of 4-formylcyclohexene. Conformations within a box interconvert via barriers that are too low to be visible in DNMR. Interconversion between conformations in different boxes occurs by half-chair ring flip and via a barrier that is high enough to be visible in DNMR
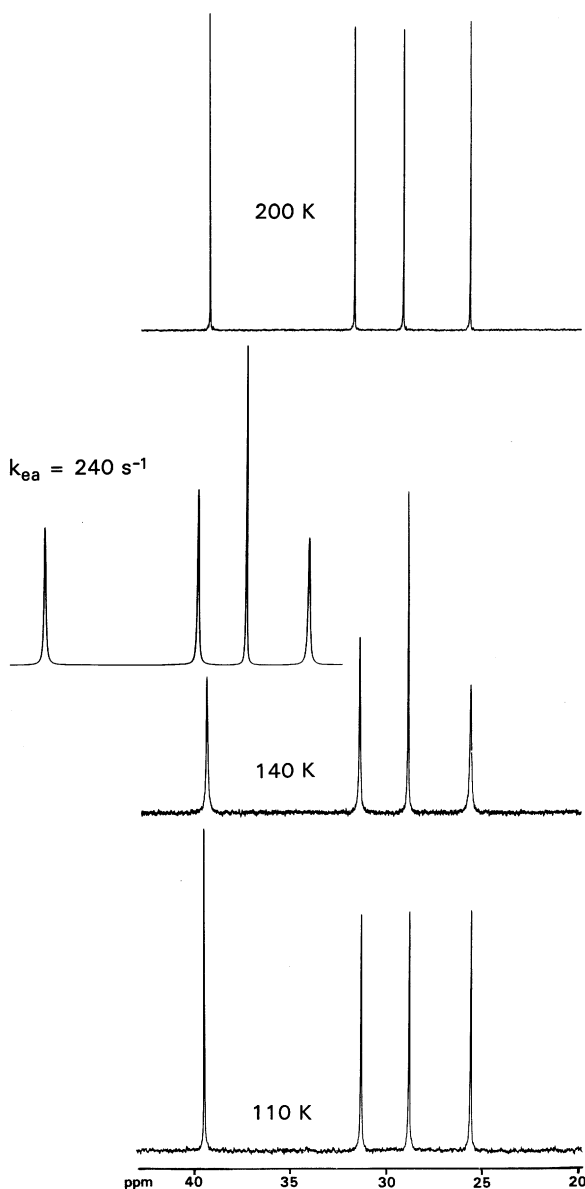
Figure 4. Experimental $^{13}C\{^1H\}$ NMR spectra (125.76 MHz) of the aliphatic carbons of 4-vinylcyclohexene (10% v/v in 50% CF_2Cl_2–50% CHF_2Cl) and a theoretical simulation at 140 K offset to the upper left. The rate constant (k_{ea}) is associated with the conversion of equatorial to axial conformations

angle is 5.4°; the C=O bond almost eclipses the C-3—C-4 bond. The torsion angle between the aldehydic C—H bond and the axial C-4—H bond is 65.8°. This torsion angle will result in a small spin–spin coupling constant between the aldehydic proton and the axial C-4 proton. In **2**, the C-5—C-4—C=O torsion angle is −1.1°; the C=O bond eclipses the C-5—C-4 bond. The torsion angle between the aldehydic C—H bond and the axial C-4—H bond is −62.6°. This torsion angle will also result in a small spin–spin coupling constant between the aldehydic

proton and the axial C-4 proton. Another equilibrium conformation (**3**) is predicted at an H—C—C=O torsion angle of 0° ($\Delta H_f = -27.82$ kcal mol^{-1}); **3** is predicted to be present at less than 1% of the concentration of **1** or **2** at 108 K, i.e. at too low a concentration to be detectable by NMR. A 360° MMX torsion angle driver calculation for formyl group rotation identified three rotation barriers at 1.73 (**1** to **3**), 1.88 (**2** to **3**) and 2.23 kcal mol^{-1} (**1** to **2**). Consistent with the NMR data, the MMX force field predicts that the equatorial conformations are dominated by two isoenergetic species (**1** and **2**) that interconvert rapidly at 108 K (Scheme 1). Owing to rapid chemical exchange, the NMR data do not allow a direct measure of the populations of the two conformations and a direct comparison with the MMX-calculated heats of formation.

With the formyl group in the axial position, the MMX force field predicts three equilibrium conformations including **4** ($\Delta H_f = -28.20$ kcal mol^{-1}) and **5** ($\Delta H_f = -27.90$ kcal mol^{-1}) as shown in Scheme 1. In **4**, the interatomic distance between oxygen and the pseudo-equatorial C-3 proton is 2.66 Å. The C-3—C-4—C=O torsion angle is 2.8°; the C=O bond essentially eclipses the C-3—C-4 bond. The torsion angle between the aldehydic C—H bond and the equatorial C-4—H bond is 63.8°. This torsion angle will result in a small spin–spin coupling constant between the aldehydic proton and the C-4 proton. In **5**, the interatomic distance between oxygen and the pseudo-axial C-6 proton is 2.62 Å. The C-5—C-4—C=O torsion angle is −14.3°; the C=O bond almost eclipses the C-5—C-4 bond. Oxygen is twisted slightly away from the pseudo-axial C-6 proton. It is apparent that **5** is destabilized relative to **4** owing to slightly enhanced non-bonded repulsions between oxygen and the pseudo-axial C-6 proton. The torsion angle between the aldehydic C—H bond and the equatorial C-4—H bond is **5** is −74.0°. This torsion angle will also result in a small spin–spin coupling constant between the aldehydic proton and the equatorial C-4 proton. Another equilibrium conformation (**6**) is predicted at an H—C—C=O torsion angle of 11.1° ($\Delta H_f = -27.15$ kcal mol^{-1}); **6** is predicted to be present at less than 0.04% of the concentration of **1** or **2** at 108 K, i.e. at much too low a concentration to be detectable by NMR. A 360° torsion angle driver calculation for formyl group rotation identified three rotation barriers at 1.2 (**5** to **6**), 2.1 (**4** to **6**) and 3.1 kcal mol^{-1} (**4** to **5**). Consistent with the NMR data, the MMX force field predicts that the axial conformations are dominated by two forms that interconvert rapidly at 108 K (Scheme 1). The NMR data do not allow a direct measure of the populations of the two conformations.

In all four dominant equilibrium conformations of 4-formylcyclohexene (Scheme 1), the MMX-calculated torsion angle between the aldehydic proton and the C-4 proton ranges from 62.6° to 74.0°. Based on the Karplus relationship, this range of torsion angles will result in

small $^3J_{HCCH}$ values (1.5–3.0 Hz) for coupling between these protons. While the aldehydic proton NMR signal did not decoalesce and formyl group rotation is fast at 108 K, the narrow aldehydic proton signal observed at high ($\Delta\nu_{1/2}$ = 1.8 Hz at 180 K) and low temperatures is consistent with small $^3J_{HCCH}$ values and is qualitatively consistent with the MMX calculations of the preferred conformations of the formyl group (Scheme 1).

4-Formylcyclohexene has been studied by using the MMP2 force field.[12] Calculations that incorporated quantum mechanical interactions between the formyl group and the carbon–carbon double bond, or neglected that interaction, produced the same preference for equatorial conformations (0.83 kcal mol)$^{-1}$, suggesting no stabilizing charge transfer from the carbonyl group to the ring double bond in the axial conformer. These calculations agree well with the MMX force field data (Table 3).

The DNMR studies described above complemented by molecular mechanics calculations allow a comprehensive description of the stereodynamics of 4-formylcyclohexene illustrated in Scheme 1. With the formyl group in the equatorial position, there are two dominant iso-energetic conformations (**1** and **2**) that interconvert rapidly at 108 K. With the formyl group in the axial position, there are two dominant conformers (**4** and **5**) with **4** slightly more stable than **5** that also interconvert rapidly at 108 K. Formyl group rotation is fast enough at 108 K so that it is invisible in DNMR. Interconversion between the axial and equatorial families of conformations via half-chair ring inversion has a barrier high enough (5.6 kcal mol)$^{-1}$ to be visible in DNMR.

Conformational preferences in 4-substituted cyclo-hexenes with polar substituents are known to be solvent dependent.[7] 4-Formylcyclohexene is no exception (see above). It is interesting that the respective percentages of axial conformations in CHF$_2$Cl, 50% CF$_2$Cl$_2$–50% CHF$_2$Cl and CF$_2$Cl$_2$ at 108 K are 23, 23 and 11%, respectively. In proceeding through this series of solvents, the polarity of the solvent system progressively decreases while the axial conformational population is the same in CHF$_2$Cl and 50% CF$_2$Cl$_2$–50% CHF$_2$Cl and then falls off in CF$_2$Cl$_2$. While non-bonded repulsions play a major role in the conformational preferences, the enhanced axial concentration in polar solvents is interesting. The observation that the concentration of axial forms does not follow the solvent polarity suggests that the solvent dependence may not be entirely due to dielectric effects and may also involve hydrogen bonding by CHF$_2$Cl.

An axial formyl group on the cyclohexane ring will experience greater non-bonded repulsions than an axial 4-formyl group on the cyclohexene ring. Therefore, it is not surprising that the free energy preference for equatorial formylcyclohexane (−0.84 kcal mol^{-1} in CD$_2$Cl$_2$)[13] is larger than that in 4-formylcyclohexene (−0.44 kcal mol^{-1} in CF$_2$Cl$_2$).

4-Vinylcyclohexene

The ^{13}C{^{1}H} NMR spectrum (125.76 MHz) of 4-vinyl-cyclohexene (10% v/v in 50% CF$_2$Cl$_2$–50% CHF$_2$Cl) at 200 K shows aliphatic carbon resonances at 26.1, 29.4, 31.8 and 39.3 ppm and olefinic carbon signals at 112.9, 127.2, 128.8 and 145.1 ppm. Below 130 K, various resonances undergo significant differential broadening and then resharpen at lower temperatures. The aliphatic carbon resonances are illustrated in Figure 4. For example, at 140 K (Figure 4), the respective widths at half-height of the aliphatic carbon resonances at 25.8, 29.0, 31.5 and 39.3 ppm are 14.3, 6.2, 9.8 and 14.1 Hz. No decoalscence of any signal into two separate resonances is observed. Two conformational exchange processes occur in 4-vinylcyclohexene: half-chair ring inversion and rotation about the vinyl—C-4 bond. Molecular mechanics calculations predict barriers to vinyl rotation that are less than 1.0 kcal mol^{-1} (see below); this process occurs at a rate too fast to be visible in DNMR even at 110 K. The barrier to half-chair ring inversion has been shown to be high enough to be visible in DNMR.[1,2,3] Therefore, this spectral behavior is best rationalized in terms of exchange between a strongly dominant family of equatorial conformations (see above) and a family of axial conformations present at concentrations that give signals below the noise level. It must be noted that the axial conformations are presents at concentrations high enough to cause exchange broadening. The noise level in the 110 K spectrum is about 1.5% of the intensity of the peak at 39.5 ppm. By employing a ratio of major to minor species of 97:3, the 140 K spectrum in Figure 4 can be simulated by invoking exchange within each of the following pairs of aliphatic carbon chemical shifts: 25.8 ppm (97%) and 22.0 ppm (3%), 28.9 ppm (97%) and 28.2 ppm (3%), 31.4 ppm (97%) and 28.8 ppm (3%), and 39.5 ppm (97%) and 35.8 ppm (3%). A progressive reduction in the population of the minor species produces less and less differential broadening and, at a population of 0.1%, all differential broadening disappears in the calculated spectrum. Based on this analysis, axial conformations are present at about 3% or less at 140 K; the lower limit on the free energy preference for the equatorial conformers is estimated to be 1.0 kcal mol^{-1} at 140 K.

MMX calculations predict a strong preference for an equatorial family of conformations in 4-vinylcyclo-hexene. With the vinyl group in the equatorial position, MMX predicts **7** to be the most stable conformer (ΔH_f = 16.04 kcal mol^{-1}). In **7**, the H*—C—C-4—H torsion angle is calculated to be 176.1°. Three other equilibrium conformations with H*—C—C-4—H torsion angles of −12°, −42° and 71° are 0.42, 0.43 and 0.76 kcal mol^{-1}, respectively, less stable than **7**. All of these equilibrium conformations interconvert by isolated rotation about the vinyl—C-4 bond via barriers that are 1.0 kcal mol^{-1} or less; rotation is fast at 110 K. A theor-

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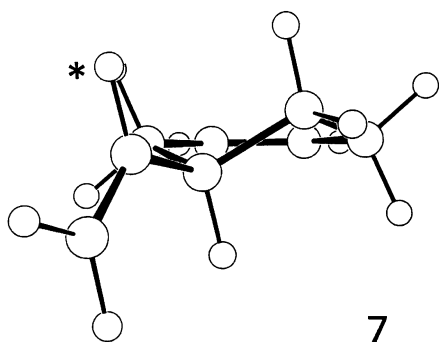
etical simulation of the vinyl methine proton NMR resonance at 200 K reveals coupling ($^3J_{HCCH}$) to the *trans* vinyl proton (17.2 Hz), to the *cis* vinyl proton (10.8 Hz) and to the C-4 proton (6.8 Hz). The coupling of the vinyl methine proton to the C-4 proton in **7** is predicted to be 11.6 Hz. The value observed at 200 K is consistent with **7** interconverting with appreciable concentrations of the other equilibrium forms in which the coupling will be much smaller (4–7 Hz). With the vinyl group in the axial position, MMX predicts two equilibrium conformations with H*—C—C-4—H torsion angles of −154° and 47° that are 3.13 and 3.78 kcal mol^{-1} respectively, less stable than **7**. The smallest calculated energy difference between an equatorial and axial form is 2.38 kcal mol^{-1}, which is substantially larger than the lower limit estimated from the NMR data. In any event, the equatorial preference for the 4-vinyl group is substantially larger than that for the 4-formyl group.

4-Methylcyclohexene

The $^{13}C\{^1H\}$ NMR spectrum (125.76 MHz) of 4-methyl-cyclohexene (10% v/v in 50% CF_2Cl_2–50% CHF_2Cl) at 200 K shows aliphatic carbon resonances at 22.9, 26.5, 29.8, 32.0 and 34.6 ppm and two olefinic carbon signals that overlap at 128.0 ppm. Below 130 K, various resonances undergo differential broadening and are resharpened at 110 K. No decoalescence into separate signals is observed. By using an approach analogous to that employed for 4-vinylcyclohexene (see above), a lower limit on the preference for equatorial 4-methylcyclohexene over the axial form is estimated at 1.0 kcal mol.$^{-1}$ From an analysis of the epoxidation rates of various methylated cyclohexenes, the preference for equatorial over axial methylcyclohexene is estimated to be 1 kcal mol^{-1}.[14]

The MMX force field predicts a 1.44 kcal mol^{-1} preference for the equatorial conformation of 4-methyl-cyclohexene. Another molecular mechanics calculation predicts a 1.04 kcal mol^{-1} preference.[15] It is apparent that the equatorial preference for methyl is also larger than that for formyl.

EXPERIMENTAL

4-Formylcyclohexene, 4-vinylcyclohexene and 4-methylcyclohexene were purchased from Aldrich Chemical. Purity was confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

The dynamic NMR spectra were recorded by using a Bruker ARX-500 NMR system at the University of Vermont. The NMR sample temperature was varied by using a Bruker BVT-2000 temperature control unit. Sample temperature was calibrated against the permanent probe thermocouple by using a copper–constantan thermocouple inserted in an NMR tube containing toluene. Temperature was accurate to ± 3 K. NMR samples were prepared in precision 5 mm tubes and sealed after four freeze–pump–thaw cycles. All spectra are referenced to tetramethylsilane at 0 ppm.

Acknowledgment

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