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STRUCTURAL STUDIES BY NUCLEAR MAGNETIC RESONANCE—XXIII

CONFORMATIONAL ANALYSIS OF SUBSTITUTED PHENYLACETALDEHYDES

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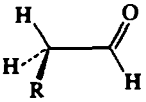
Abstract—The vicinal spin–spin coupling constants between the aldehydic and α-protons of phenylacetaldehyde, *p*-methylphenylacetaldehyde, *p*-methoxyphenylacetaldehyde, *p*-chlorophenylacetaldehyde, and 2,6-dichlorophenylacetaldehyde were studied at 60 MHz as a function of temperature and solvent. The following conclusions were drawn. (1) A threefold barrier to rotation about the sp^2–sp^3 carbon–carbon bond best fits the data for the substituted phenylacetaldehydes. (2) The stability of the rotamer, where the phenyl group eclipses the carbonyl group, increases with increasing solvent dielectric constant. (3) The free energy and enthalpy values for $1 \rightleftharpoons 2$ are solvent dependent, being more negative in solvents of high dielectric constant. (4) Local dipole–dipole interactions are more important than overall dipole–dipole interactions in determining rotamer stability.

Previously, we have discussed the conformational analysis of several aldehydic systems and have interpreted the results in terms of dipole–dipole interactions.[1-3] We pointed out that nonbonded repulsions and dipole-induced dipole interactions are often of minor significance in determining the relative stabilities of rotamers **1** and **2**. In order to understand more fully the importance of dipole–dipole interactions in determining rotamer stability, we investigated substituted phenylacetaldehydes. Two possibilities arise. (1) Overall dipole–dipole interactions are important in determining rotamer stability (ie phenyl group and substituent). (2) Local dipole–dipole interactions are important (i.e. substitution on phenyl group has little or no effect on rotamer stability). In this paper, we wish to discuss the conformational analysis of substituted phenylacetaldehydes and the importance of local dipole–dipole interactions in determining rotamer stability.



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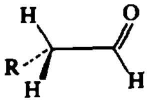

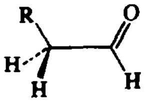

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RESULTS

Spin–spin coupling constants. The vicinal spin–spin coupling constants between the aldehydic and methylene protons of several substituted phenyl-acetaldehydes in 5% solutions in various solvents are summarized in Table 1. All values are averages of six to ten measurements with a precision of ±0·03 Hz. To insure internal accuracy and consistency, values were always checked against those of acetaldehyde 2·85, 2·88 and 2·90 Hz at 36, 0 and −30° respectively.[4]

As with the coupling constants of monosubstituted alkylacetaldehydes,[1] those of the substituted phenylacetaldehydes are smaller than that of acetaldehyde. The coupling constants are found to decrease with increasing solvent polarity. When compared in the same solvent, the coupling constants decrease as the substituent on the phenyl group becomes more electronegative.

The data in Table 2 demonstrate the effect of temperature on the vicinal spin–spin coupling constants, J_{HH}, of the substituted phenylacetaldehydes. The coupling constants of phenylacetaldehyde and *p*-methylphenylacetaldehyde decrease with increasing temperature in solvents of low dielectric constant and increase with increasing temperature in solvents of high dielectric constant. The coupling constant of *p*-methoxyphenylacetaldehyde is constant in ethyl ether and increases with increasing temperature in solvents of higher dielectric constant. The coupling constants of *p*-chlorophenylacetaldehyde and 2,6-dichlorophenylacetaldehyde increase with increasing temperature in all solvents studied.

Table 1. Vicinal spin–spin coupling constants[a] of substituted phenylacetaldehydes

Solvent[b]	J_{HH}, Hz $PhCH_2CHO$	 *p*-CH_3PhCH_2CHO	 *p*-CH_3OPhCH_2CHO	 *p*-$ClPhCH_2CHO$	 2,6-Cl_2PhCH_2CHO
Cyclohexane	2·46	2·52		2·20	1·19
trans-Decalin	2·48	2·50		2·18	1·22
CCl_4		2·51			1·18
$(CH_3CH_2)_2O$	2·43	2·50	2·50	2·13	1·14
THF	2·33		2·41	2·00	1·04
$CHCl_3$		2·45			1·19
CH_2Br_2	2·28	2·30	2·27	2·02	1·15
CH_2Cl_2		2·27			1·10
$(CH_3)_2NCHO$	2·09	2·15	2·16	1·79	·76
C_6H_5CN	2·14	2·17	2·20	1·83	·97

[a] Values at 38 ± 2°. [b] 5% solutions.

Table 2. Temperature dependence of the vicinal spin–spin coupling constant of substituted phenylacetaldehydes

Solvent[a]	J_{CH-CHO}, Hz −30°	−15°	0°	15°	38°	60°	90°	120°
				$C_6H_5CH_2CHO$				
Cyclohexane				2·44	2·46	2·43	2·38[b]	
trans-Decalin	2·45	2·46	2·47	2·46	2·48	2·44	2·44	2·39
$(CH_3CH_2)_2O$	2·43	2·44	2·42	2·45	2·43			
CH_2Br_2	2·09	2·13	2·17	2·21	2·28	2·28	2·28	
$(CH_3)_2NCHO$	1·84	1·85	1·96	1·99	2·09	2·09	2·12	2·14
				p-$CH_3C_6H_4CH_2CHO$				
Cyclohexane				2·56	2·52	2·51	2·47[b]	
trans-Decalin	2·54	2·56	2·56	2·54	2·50	2·48	2·44	2·44
$(CH_3CH_2)_2O$		2·51	2·48	2·49	2·50			
CH_2Br_2	2·00	2·17	2·18	2·26	2·30	2·30	2·24	
$(CH_3)_2NCHO$	1·85	2·01	2·06	2·08	2·15	2·16	2·17	2·20
				p-$CH_3OC_6H_4CH_2CHO$				
$(CH_3CH_2)_2O$	2·53	2·50	2·53	2·53	2·50			
CH_2Br_2	2·14	2·22	2·21	2·28	2·27	2·32	2·37	
$(CH_3)_2NCHO$	2·05	2·04	2·10	2·12	2·16	2·18	2·23	2·24
				p-$ClC_6H_4CH_2CHO$				
Cyclohexane				2·13	2·20	2·19	2·17[b]	
trans-Decalin			2·13	2·13	2·18	2·20	2·21	2·20
$(CH_3CH_2)_2O$			1·92	2·05	2·13			
CH_2Br_2	1·82	1·80	1·79	1·98	2·02	2·06	2·09	
$(CH_3)_2NCHO$	1·47	1·54	1·53	1·60	1·79	1·84	1·88	1·89
				2,6-$Cl_2C_6H_3CH_2CHO$				
Cyclohexane				1·13	1·19	1·23	1·27[b]	
trans-Decalin	·90	·98	1·12	1·13	1·22	1·24	1·28	1·35
$(CH_3CH_2)_2O$	·87	·98	1·03	1·02	1·14			
CH_2Br_2	·82	·93	·98	1·08	1·15	1·20	1·27	
$(CH_3)_2NCHO$			·56	·62	·76	·86	·97	1·05

[a] 5% solutions. [b] Value at 80°.

The data summarized in Tables 1 and 2 may be interpreted in terms of **1a**, **1b** and **2** as the equilibrium configurations of substituted phenylacetaldehydes. Assuming $J_t > J_g$, where J_t is the trans coupling constant and J_g is the gauche, we deduce that the observed average vicinal spin–spin coupling constants would be temperature independent if **1a**, **1b** and **2** were isoenergetic, they would decrease with increasing temperature, if **1a** were more stable than **2** and would increase with increasing temperature, if **1a** were less stable than **2**. From the temperature dependence of the spin–spin coupling constants, we conclude: (a) In solvents of low dielectric constant, the most stable rotamer of phenylacetaldehyde, *p*-methylphenylacetaldehyde, and *p*-methoxyphenylacetaldehyde is **1a**, while in solvents of high dielectric constant, **2** is the more stable rotamer. (b) Regardless of solvent dielectric constant, **2** is the more stable rotamer for *p*-chlorophenylacetaldehyde and 2,6-dichlorophenylacetaldehyde.

Rotamer populations and free energy differences, $\Delta G°$, between individual rotamers can be calculated from Eqns (1) and (2), respectively, where p is the fractional population of **1** (**1a** + **1b**) and $(1-p)$ that of **2**. Enthalpy differences, $\Delta H°$, between **1** and **2** may be obtained from plots of log K_{eq} vs $1/T$, where K_{eq} is given by Eqn (3).

$$J_{obs} = p(J_t + J_g)/2 + (1-p)J_g \quad (1)$$

$$\Delta G° = -RT \ln [(J_t + J_g - 2J_{obs})/(J_{obs} - J_g)] \quad (2)$$

$$K_{eq} = 2(1-p)/p \quad (3)$$

Table 3. Solvent dependence of the relative rotamer populations[a] of substituted phenylacetaldehydes

Solvent	%, 2 $PhCH_2CHO$	*p*-CH_3PhCH_2CHO	*p*-CH_3OPhCH_2CHO	*p*-$ClPhCH_2CHO$	2,6-Cl_2PhCH_2CHO
Cyclohexane	32	28		34	38
Trans-Decalin	32	28		34	37
$(CH_3CH_2)_2O$	33	28	31	36	40
THF	36		33	39	42
CH_2Br_2	37	34	37	39	39
$(CH_3)_2NCHO$	43	38	41	45	50
C_6H_5CN	41	38	39	44	44

[a] All values calculated for 38°.

Calculation of rotamer populations, K_{eq}, $\Delta G°$ and $\Delta H°$ requires knowledge of the parameters J_t and J_g. In compounds where large changes in the magnitude of the coupling constant are observed, limits may be set for J_t and J_g. However, as in the compounds studied here, when only small changes are observed in the coupling constant, such estimates are not easily made.

Eqn (4) relates the experimental coupling constant to J_t and J_g, either

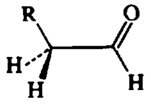
$$J_{obs} = (1/3)(J_t + 2J_g) \qquad (4)$$

when the three rotamers, **1a**, **1b** and **2**, are equally populated or at the state of free rotation—usually at very high temperatures—about the sp^2-sp^3 carbon–carbon bond. For phenylacetaldehyde, *p*-methylphenylacetaldehyde, *p*-methoxyphenylacetaldehyde, *p*-chlorophenylacetaldehyde, and 2,6-dichlorophenylacetaldehyde, J_{obs} of Eqn (4) obtained from plots of J_{obs} vs temperature is 2·40, 2·30, 2·40, 2·20 and 1·35 Hz, respectively. Since J_{obs} of eqn (4) for acetaldehyde is 2·85 Hz and good estimates for J_t and J_g are 7·6 and 0·5 Hz,[1] respectively, J_{obs} for the substituted phenylacetaldehydes may be used to estimate corrections necessary to apply to the data obtained for these compounds in order to permit the use of J_t and J_g of acetaldehyde in Eqns (1) and (2).

The effect of solvent dielectric constant on the relative rotamer populations, calculated from eqn (1), for the substituted phenylacetaldehydes are shown in Table 3. Inspection of the results reveals an increase in the concentration of the more polar rotamer, **2**, as the solvent dielectric constant increases. The same effect is seen in terms of the free energy differences, $\Delta G°$, between rotamers **1a** and **2** that were calculated from Eqn (2) (Table 4). Table 5 summarizes the enthalpy differences, $\Delta H°$, between the various rotamers calculated from reasonably linear plots of log K_{eq} vs $1/T$. From arguments already discussed,[1] these values should not be taken as better than ±20%.

DISCUSSION

In interpreting our results, we have assumed a dominant threefold barrier to rotation about the sp^2-sp^3 carbon–carbon bond. Before discussing these results, we wish to consider the question of their compatibility with a dominant twofold barrier to rotation. Assuming that **2** and **3**



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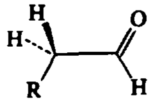

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are the equilibrium configurations the relevant vicinal spin–spin coupling constants would be $J_g(J_{60°})$ for **2** and $J_{120°}$ for **3**. For a twofold barrier, Eqn (4) then becomes Eqn (5).

$$J_{obs} = (1/2)(J_g + J_{120°}) \qquad (5)$$

From the data for the substituted phenylacetaldehydes, it can be seen that J_g must be equal to or smaller than 1·84, 1·85, 2·05, 1·47 and 0·52 Hz for phenyl-, *p*-methylphenyl-, *p*-methoxyphenyl-, *p*-chlorophenyl-, and 2,6-dichlorophenylacetaldehyde, respectively. If J_g and $J_{120°}$ are assumed to have the same sign, then $J_{120°}$ would have to be equal to or greater than 2·96, 2·76, 2·74, 2·92 and 2·48 Hz, respectively. These results are unreasonable, since J_g and $J_{120°}$ are expected to have similar values.[5] Since J_g for these compounds is certainly less than 1 Hz, the discrepancy between J_g and $J_{120°}$ is even larger than that calculated by using the minimum values of the observed coupling constant. If J_g and $J_{120°}$ are assumed to be of opposite signs, the discrepancy becomes even larger.

In order to prevent any misinterpretation of our results, we reemphasize[1] that, while we consider rotamers **1** and **2** as perfectly eclipsed, NMR gives no accurate assessment of the various dihedral angles. In fact, it may be the variation of dihedral angle—along with changes in s-character and energy wells—that causes the differences

Table 4. Solvent dependence of the free energy difference, $\Delta G°$, between rotamers of substituted phenylacetaldehydes

	$\Delta G°$, cal mol^{-1}, for **1a**⇌**2**				
Solvent[a]	$PhCH_2CHO$	p-CH_3PhCH_2CHO	p-CH_3OPhCH_2CHO	p-$ClPhCH_2CHO$	2,6-Cl_2PhCH_2CHO
Cyclohexane	+40	+170		−20	−130
trans-Decalin	+50	+150		−20	−100
$(CH_3CH_2)_2O$	+10	+150	+70	−80	−180
THF	−70		+10	−160	−230
CH_2Br_2	−110	−20	−100	−160	−160
$(CH_3)_2NCHO$	−240	−130	−210	−310	−430
C_6H_5CN	−210	−110	−150	−280	−280

[a] 5% solutions.

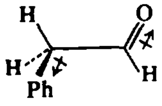
Table 5. Enthalpy differences, $\Delta H°$, between rotamers of substituted phenylacetaldehydes

	$\Delta H°$, cal mol^{-1}, for **1a**⇌**2**				
Solvent[a]	$PhCH_2CHO$	p-CH_3PhCH_2CHO	p-CH_3OPhCH_2CHO	p-$ClPhCH_2CHO$	2,6-Cl_2PhCH_2CHO
Cyclohexane	+220	+350		0	−540
trans-Decalin	0	+280		0	−570
$(CH_3CH_2)_2O$	0	0	0	−1100	−630
THF			0	−620	−890
CH_2Br_2	−420	−430	−360	−700	−790
$(CH_3)_2NCHO$	−520	−340	−350	−720	−1020
C_6H_5CN	−360	−310	−370	−670	−830

[a] 5% solutions.

observed between the temperature independent values of the substituted phenylacetaldehydes.

Effect of solvent polarity on rotamer stabilities. The increase in the rotamer ratio, **2**/**1**, for phenylacetaldehyde, reflected by the data in Tables 3 and 4, as the dielectric constant and polarity of the medium increases, is reasonable in view of the higher dipole moment of rotamer **5** relative to that of **4**.



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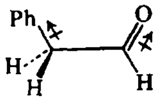

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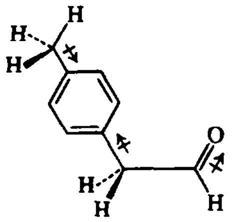
Consideration of the dipoles in *p*-methylphenylacetaldehyde indicates that the dipoles, other than that of the carbonyl, should almost completely cancel, as shown in **6**.



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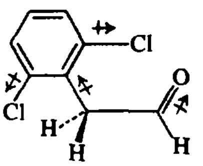
Therefore, if the overall dipole of the molecule in the solvent were of major importance in determining rotamer stability, it would be expected that the rotamer ratio, **2**/**1**, should be invarient with solvent dielectric constant. If, however, only local dipole–dipole interactions were important, i.e. those associated with the atoms directly bonded to the C_{sp^2}–C_{sp^3} bond, the population and the increase in population of **2** with increasing solvent dielectric constant should parallel that observed for phenylacetaldehyde. The latter is the case.

In *p*-methoxyphenylacetaldehyde, the overall dipole will depend on the magnitude and direction of the dipole of the methoxy group. From the work of Taft and coworkers,[6] whereby Hammett σ_p values have been separated into σ_I and σ_R values, the contribution due to resonance (donation of electrons) is more than twice as large as that due to induction (withdrawal of electrons). Comparison of the dipole moments for anisole,[7] chlorobenzene,[8] bromobenzene,[9] *p*-chloroanisole,[10] and *p*-bromoanisole[11] (1·16, 1·52, 1·51, 2·24 and 2·23 D respectively) also indicates that the dipole arising from the methoxy group is directed towards the phenyl group. This indicates that **1** should have a higher overall dipole than **2** and therefore, if overall dipole–dipole interactions were important, a decrease in the population of **2** would be expected as solvent dielectric constant increases. This is not the case, rather, the observed trends in populations, free energy differences, and enthalpy differences are comparable to those of phenylacetaldehyde. This is consistent with local dipole–dipole interactions being a major factor in determining rotamer stability.

For *p*-chlorophenylacetaldehyde, Taft's σ_I and σ_R values indicate that the withdrawal of electrons by induction is about twice as important as the resonance effect.[6] Comparison of the dipole moments for chlorobenzene,[8] nitrobenzene,[12] toluene,[8] *p*-chlorobenzene,[7] and *p*-chlorotoluene,[13] (1·52, 3·84, 0·4, 2·55 and 1·74 D, respectively) indicates that the dipole for the chloro group is directed away from the phenyl. Therefore, if overall dipole–dipole interactions were a major factor in determining rotamer stability, the population of **2** in solvents of high dielectric constant for *p*-chlorophenylacetaldehyde should be greater than for phenylacetaldehyde. However, consistent with local dipole–dipole interactions being of major importance in determining rotamer stability, the populations, free energy differences, and enthalpy differences are found to be similar to those of phenylacetaldehyde.

The important dipoles for conformer **2** of 2,6-dichlorophenylacetaldehyde are shown in **7**. If overall dipole–dipole interactions were controlling rotamer stabilities, then the population of **2** should be smaller for 2,6-dichlorophenylacetaldehyde than for phenylacetaldehyde. Furthermore, as the solvent dielectric constant increased, the population of **2** should decrease. This is not the case.



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The preceeding discussion shows that local dipole–dipole interactions are more important in determining rotamer stability than are overall dipole–dipole interactions. In retrospect, such a finding is reasonable, in view of the expected ability of solvent to interact with the dipoles of the phenyl ring and its substituents equally well in either conformer **1** or **2**.

As pointed out previously,[1–3] in solvents of high dielectric constant ΔG° values may better reflect the enthalpy differences between rotamers whose dipole moments differ greatly, than do the calculated ΔH° values, since increasing temperature decreases solvent dielectric constant which, in turn, decreases the ratio **2**/**1** and leads to the calculation of too negative ΔH° values.

EXPERIMENTAL

Phenylacetaldehyde (Aldrich Chemical Co.) was commercially available. *p-Methylphenylacetaldehyde* was prepared by a combination of known procedures.[14,15] To conc H_2SO_4 (90 g) cooled in an ice bath, was added *p*-methylbenzyl cyanide (25 g, 0·19 mol) with stirring over a period of 0·5 hr, followed by 2 - methyl - 2,4 - pentanediol (21·3 g, 0·18 mol) added over 2 hr. This mixture was poured over ice (180 g), half-neutralized with 40% NaOH and extracted three times with $CHCl_3$ (100 ml). The pH was adjusted to 10 and the product extracted with ether and dried (K_2CO_3). After evaporation 2 - (*p* - methylbenzyl) - 4,4,6 - trimethyl - 5,6 - dihydro - 1,3(4*H*) - oxazine (8·5 g, 19·6%) was obtained as a yellow oil which solidified on distillation (84–90°/0·3 mm). The product was dissolved in a mixture of 200 ml of THF and 200 ml of 95% EtOH, cooled to −40° and 9 N HCl and sodium borohydride solution (7·6 g, in 15 ml of water containing 2 drops of 40% NaOH) were added alternatively, keeping the pH between 6 and 8. The reaction mixture was cooled for an additional 2 hr, 200 ml of water was added and the solution was made basic with 40% NaOH. The layers were separated and the aqueous layer extracted twice with ether. The combined organic layers were washed twice with 200 ml of sat. NaCl soln and dried (K_2CO_3). After evaporation crude 2 - (*p* - methylbenzyl) - 4,4,6 - trimethyltetrahydro - 1,3 - oxazine was added dropwise to 300 ml of water containing 100 g of oxalic acid. The resulting aldehyde was steam distilled under helium, the distillate saturated with NaCl and extracted three times with 150 ml portions of pentane. Distillation of the dried pentane extracts yielded *p*-methylphenylacetaldehyde (1·6 g, 11 mmol, 6·6%, 44–46°/0·5 mm).

p-*Methoxyphenylacetaldehyde* was prepared by a known procedure.[16] To a suspension of yellow mercuric oxide (22 g) in a solution of *p*-methoxystyrene (10 g, 0·74 mol), 100 ml of ether and 10 ml of water, was added small portions of iodine (25 g) during 1 hr. The solution was filtered, washed twice with sat. sodium thiosulfate solution and diluted with 50 ml of EtOH. After the removal of ether and addition of 100 ml of sat. sodium bisulfite, the solution was stirred for 1 h and the bisulfite adduct filtered and washed with ether. After addition of 100 ml of sat. $NaHCO_3$ to an aq. solution of the adduct, the solution was stirred for 1 hr at 0° and then extracted with ether, dried (Na_2SO_4) and evaporated to give *p*-methoxyphenylacetaldehyde (3·9 g, 26 mmol, 35%).

p-*Chlorophenylacetaldehyde and* 2,6-*dichlorophenylacetaldehyde* were prepared by a known procedure.[17] The following is a typical preparation. To freshly distilled *p*-chlorostyrene (10 g, 72·5 mmol) dissolved in CH_2Cl_2 (250 ml) and cooled to 0° was added dropwise freshly distilled chromyl chloride (12·6 g, 6·6 ml, 82 mmol) dissolved in CH_2Cl_2 (125 ml). After 1 hr, Zn dust (6·10 g, 94 mmol) was added, followed, after an additional 15 min of stirring, by 37 ml of water and 15 g of ice. The mixture was allowed to reach room temperature and then steam distilled until 5 l. of distillate were collected, which was extracted with an equal volume of CH_2Cl_2, dried ($MgSO_4$) and evaporated. The resulting oil was distilled, yielding *p*-chlorophenylacetaldehyde (0·48 g, 3·1 mmol, 4·3%) as a colourless solid (b.p. 75–78°/0·6 mm).

2,6-*Dichlorophenylacetaldehyde* was obtained similarly as a colourless solid (b.p. 95–98°/0·2 mm) from 2,6-dichlorostyrene.

NMR spectra were determined at 60 MHz on a Model A56/60D spectrometer (Varian Associates, Palo Alto, Calif.), equipped with a variable-temperature probe and a V-6040 variable-temperature controller.

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