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EVIDENCE FOR THE PRESENCE OF CH–π-INTERACTED *ap*-CONFORMERS OF BENZYL FORMATES

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In order to examine the preferred conformations of benzyl, 1-phenylethyl and cumyl formates, lanthanoid-induced shifts (LIS) of ^{1}H and ^{13}C NMR and difference NOE spectra of these esters were measured. The measurements showed that a folded conformer capable of forming intramolecular CH–π interaction are predominant with all three series of formate esters. The LIS and other experiments suggested the coexistence of considerable amounts of extended conformers, however. As the ester group is enforced to take supposedly unfavourable *ap*-conformation in the CH–π contiguous folded conformer, the predominance of the conformer was a surprise and needed explanation. The NOE experiments on a series of *para*-substituted benzyl formates, $XC_6H_4CH_2OCHO$ ($X = CH_3O, CH_3, H, Cl, NO_2$), showed that the enhancement of aromatic proton signals (*ortho* and *meta*) induced by the irradiation of formyl proton increases gradually as the substituent becomes more electron donating, whereas the enhancement of benzylic (α) proton signal remains constant irrespective of the nature of the substituent. This can be explained by assuming that the CH–π contiguous folded conformer is in equilibrium with the extended conformer. The trend of the substituent effect supports the hydrogen bond-like nature of the CH–π interaction. A similar trend was also observed with substituted 1-phenylethyl formates. Hence the unexpected stability of the *ap*-conformer of benzyl formates could be ascribed to the stabilization due to the CH–π interaction.

INTRODUCTION

Since the success of the bulk-repulsive concept,[1] organic chemists have been accustomed to think that the most stable conformation of a molecule should be the least crowded one in which the bulkiest groups occupy the positions most remote from each other. Thus, an extended conformation is expected to be the most stable. However, several examples that apparently violate this concept have been discovered in conformational studies in recent years. Carter and co-workers[2,3] showed that 1,3,5-trineopentylbenzene favourably takes a conformation with its three *tert*-butyl groups on the same face of its benzene ring.

Our previous investigations also showed that the alkyl/phenyl synclinal conformer is usually more predominant than the alkyl/phenyl antiperiplanar conformer for a series of alkyl 1-phenylethyl compounds ArCHMe—X—R (where X = SO,[4,5] CHOH[6,7] and C=O[8]). A similar conformational preference has been demonstrated with many alkyl benzyl compounds $ArCH_2$—X—R. It appears that the folding tendency of the chain is general in a wide variety of aralkyl molecules. The preference for an alkyl/aryl contiguous (i.e. usually synclinal) conformation has been rationalized by assuming that an attractive interaction is operating between the alkyl group and aromatic π-electrons in these compounds.[9–12] Dispersion forces are certain to contribute to a large extent to such attractive interactions.[10] However, several experimental facts indicated the similarity between CH–π interactions and hydrogen bonding.[5,13,14] In order to elucidate the nature of the attractive CH–π interaction, the substituent effects on the relative population of the interacted conformer and on the energy of interaction have been examined with isopropyl 1-phenylethyl ketones,

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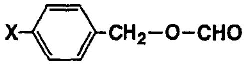
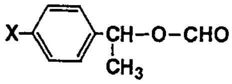
$XC_6H_4CHMe{-}COCDMe_2$.[11,13] The results showed that the interaction becomes more favourable as the substituent on the aromatic ring becomes more electron donating, suggesting that the CH–π interaction might be hydrogen bond-like.

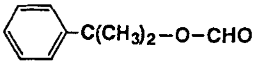
In this paper, we report the preferred conformations of several substituted benzyl formates (**1**–**3**) and give another further evidence for the hydrogen bond-like nature of the CH–π interaction by examining the electronic substituent effect on NOE.



1_a: X = H
1_b: X = CH_3O
1_c: X = CH_3
1_d: X = Cl
1_e: X = NO_2



2_a: X = H
2_b: X = CH_3
2_c: X = Cl



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RESULTS AND DISCUSSION

The lanthanoid-induced shifts (LIS)[15] were determined with $0{\cdot}2\ \mathrm{mol\,l^{-1}}$ chloroform solutions of benzyl formates by the addition of $Eu(fod)_3$. The results are given in Table 1 for substituted benzyl formates (**1**) and in Table 2 for substituted 1-phenylethyl (**2**) and α-cumyl (**3**) formates.

In the LIS experiments, the probable geometry of the substrate molecule can be deduced as the one giving the minimum value for the agreement factor (*AF*) [defined by equation (1)]:[16]

$$AF=\left\{\sum\,[(\mathrm{LIS^{obs}})_i-(\mathrm{LIS^{calc}})_i]^2\Big/\sum\,(\mathrm{LIS^{obs}})_i^2\right\}^{1/2} \tag{1}$$

where $(\mathrm{LIS^{obs}})_i$ and $(\mathrm{LIS^{calc}})_i$ refer to the observed and the calculated LIS values for *i*th nucleus, respectively. In order to find the smallest *AF* value, systematic trial-and-error calculations were carried out on the test conformations generated by rotating a pivot bond at given intervals for the torsional angle (ω).

$\mathrm{LIS^{calc}}$ was obtained by using the McConnell–Robertson equation:[17]

$$\mathrm{LIS^{calc}}=K(3\cos^2\chi_i-1)r_i^{-3} \tag{2}$$

where r_i and χ_i are the distance between the lanthanoid

Table 1. Lanthanoid-induced shifts ($\Delta\delta/c$ in ppm $\mathrm{l\,mol^{-1}}$) of benzyl formates (**1**)

		1a (X = H)	**1c** (X = *p*-Me)	**1b** (X = *p*-MeO)	**1e** (X = *p*-NO_2)
^1H	H_{formyl}	12·0	10·9	10·8	3·62
		(1·00)	(1·00)	(1·00)	(1·00)
	H_α	7·42	6·84	6·73	2·13
		(0·62)	(0·68)	(0·67)	(0·59)
	H_o	3·10	2·80	2·99	0·84
		(0·26)	(0·26)	(0·28)	(0·23)
	H_m	0·96	1·15	1·17	0·53
		(0·080)	(0·10)	(0·11)	(0·15)
	$H_{p\text{-Me}}$	—	0·52	0·58	—
			(0·047)	(0·54)	
^{13}C	C_{formyl}	19·3	17·3	17·3	5·70
		(1·00)	(1·00)	(1·00)	(1·00)
	C_α	8·37	7·64	7·83	1·83
		(0·43)	(0·44)	(0·45)	(0·33)
	C_{ipso}	3·69	1·73	3·39	[a]
		(0·19)	(0·10)	(0·20)	
	C_o	3·22	2·98	3·25	[a]
		(0·17)	(0·17)	(0·19)	
	C_m	1·66	1·64	1·85	[a]
		(0·086)	(0·095)	(0·11)	
	$C_{p\text{-Me}}$	—	0·57	0·72	—
			(0·033)	(0·042)	

[a] Not determined.

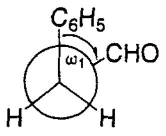
Table 2. Lanthanoid-induced shifts ($\Delta\delta/c$ in ppm l mol^{-1}) of 1-phenylethyl and cumyl formates (**2** and **3**, respectively)

		2a (X = H)	**2b** (X = *p*-Me)	**2c** (X = *p*-Cl)	**3** (X = H)
^{1}H	H_{formyl}	16·8 (1·00)	17·1 (1·00)	15·6 (1·00)	12·1 (1·00)
	H_α	12·9 (0·76)	13·1 (0·77)	11·7 (0·75)	—
	$H_{\alpha\text{-Me}}$	4·65 (0·20)	5·07 (0·30)	4·38 (0·28)	5·09 (0·42)
	H_o	4·37 (0·26)	4·65 (0·27)	4·14 (0·27)	5·06 (0·42)
	H_m	1·61 (0·095)	1·76 (0·10)	1·45 (0·093)	4·95 (0·41)
	$H_{p\text{-Me}}$	1·35 (0·080)	1·00 (0·058)	—	—
^{13}C	C_{formyl}	31·7 (1·00)	27·0 (1·00)	25·5 (1·00)	25·4 (1·00)
	C_α	14·1 (0·44)	12·4 (0·45)	11·1 (0·44)	11·5 (0·45)
	$C_{\alpha\text{-Me}}$	6·40 (0·20)	5·49 (0·20)	4·90 (0·19)	5·36 (0·21)
	C_{ipso}	6·58 (0·21)	3·22 (0·12)	5·16 (0·20)	7·67 (0·30)
	C_o	5·42 (0·17)	4·70 (0·18)	4·35 (0·17)	6·02 (0·24)
	C_m	3·23 (0·10)	2·76 (0·10)	2·54 (0·10)	3·73 (0·15)
	$C_{p\text{-Me}}$	—	1·00 (0·037)	—	—

ion (Eu^{3+}) and the *i*th nucleus (X_i) and the angle $O_{carbonyl}$—Eu—X_i, respectively. According to the previous LIS experiments, we assumed that the lanthanoid ion was coordinated on the carbonyl oxygen exclusively.[18]

As reported previously,[6–8] we used the C_{ipso}(Ar)—C_α—X—C_R torsional angle (ω) as the criterion for the presence of the CH–π interacted conformation, i.e. the interaction is possible when ω is less than 70°.[6–8] The *AF* values calculated as a function of this torsional angle ω allowed us to find the most probable conformation as the one giving the smallest *AF* value. The most (and the second) probable conformations from LIS were then examined by this criterion, and the preference of a CH–π-interacted conformer was evaluated. In the case of benzyl formates, however, the CH–π-interacted conformation can be realized only when the torsional angles about both the C_α—O and O—C_{formyl} bonds are properly adjusted so as to take a CH–π contiguous conformation.

Thus, *AF* values of *p*-methylbenzyl formate (**1c**) were plotted two-dimensionally as a function of C_{ipso}(Ar)—C_α—O—C_{formyl} and C_α—O—C_{formyl}=O torsional angles (ω_1 in **4** and ω_2 in **5**, respectively) in order to find the probable conformations (Figure 1). Geometric parameters necessary for the calculations were generated by rotating the relevant groups of the MM2-optimized extended conformation (**D**). As the number of LIS-observed nuclei is small in this series, the *AF* map from the LIS experiments did not give any sharp minimum, but showed steep maxima around the *sp*(ω_1),*sp*(ω_2)-conformation. Conformation **A**, which was predicted to be the most stable by MM2 calculations, was rejected because of its high *AF* value. Overall, the conformations **B**, **C** and **D** were compatible with the LIS data.



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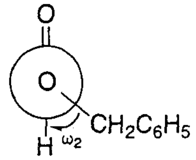

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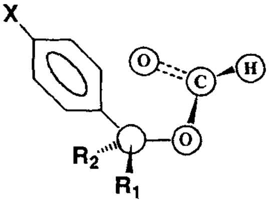
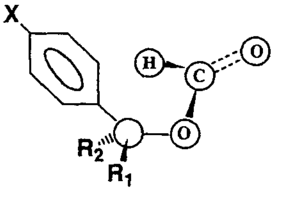
Our previous studies showed that the most probable



(A)



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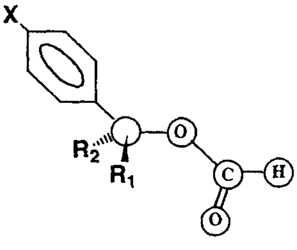

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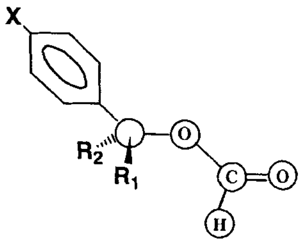

(D)

conformation agrees with one of the potential energy minima from MM2 calculations in almost all cases investigated.[9,10] This allows us to use the MM2-optimized conformations **A–D** as the test conformations for the *AF* calculations on other formates so as to avoid the repeated use of the laborious two-dimensional trial-and-error calculations on all series of formate esters. The PM3 steric energies for the four possible conformers of unsubstituted benzyl formate (**1a**) and the *AF* values for those of several typical compounds are given in Table 3. The *AF* values for all the formates investigated are consistent with the two-dimensional *AF* surface for **1c** (Figure 1).

Although the CH/Ph contiguous folded *ap* (antiperiplanar) conformers (**B**) of benzyl and 1-phenylethyl formates correspond to the second and the third most stable energy minima, respectively, from MM2 calculations, the LIS suggested them to be considerably populated conformers. Both MM2 and PM3 calculations showed that the hydrogen atom of the formyl group of conformer **B** lies just above the aromatic ring

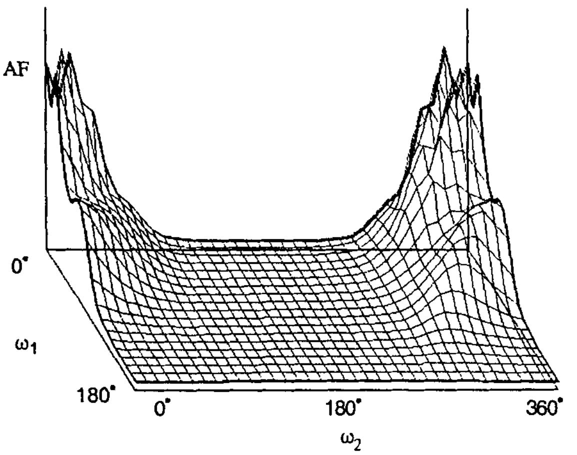

Figure 1. Two-dimensional *AF* map of *p*-methylbenzyl formate (**1c**) as a function of the $C_{ipso}(Ar)$—C_α—O—C_{formyl} (ω_1) and C_α—O—C_{formyl}=O (ω_2) torsional angles

Table 3. Agreement factors (*AF*) and PM3 energies (in kcal mol^{-1}) for the four possible conformers **A–D** of benzyl formates $HCO—O—CR_1R_2—C_6H_4X$[a]

HCO—O—CR$_1$R$_2$—C$_6$H$_4$X				Conformer				
No.	R$_1$	R$_2$	X	**A**	**B**	**B′**	**C**	**D**
Conformation: About C_{CHO}—O—C_α—C_{ipso} (ω_1) About O=C—O—C_α (ω_2)				*sc* *sp*	*sc* *a$_t$*	*sp* *ap*	*ap* *sp*	*ap* *ap*
1a	H	H	H	4·25 (0·00)	0·31 (0·91)	—	0·32 (0·94)	—
1b	H	H	CH$_3$	2·30	0·28	—	0·26	0·28
1c	H	H	CH$_3$O	1·617 (0·000)	0·286 (0·845)	0·285	0·289 (0·891)	0·312 (2·990)
1e	H	H	NO$_2$	1·05	0·34	—	0·37	—
2a	H	CH$_3$	H	1·89 (0·00)	0·31 (0·36)	—	0·88 (0·24)	—
3a	CH$_3$	CH$_3$	H	2·04 (1·90)	0·44 (0·00)	—	0·50 (1·20)	—

[a] PM3 energies of the conformers are given in parentheses.

and is favourable to have an intramolecular CH–π interaction [the C_{ortho}—C_{ipso}—C_α—O torsional angle (ω_3) was calculated to be 76·5° in the PM3-optimized conformer **B** of benzyl formate]. The folded *ap*-conformer (**B**) was computed to be 3·47 kcal mol^{-1} (1 kcal = 4·184 kJ) less stable than the most stable Ph/C=O contiguous conformer (folded *sp*, **A**) for benzyl formate by MM2. This discrepancy is far larger than the 0·5 kcal mol^{-1} which is generally accepted as the error of the force-field calculations. Therefore, the energies of these conformers were estimated by another method.

The PM3 molecular orbital calculation[19] succeeded in reducing the discrepancy between the calculated and the observed conformational preference (Table 3). The calculations on the conformers of benzyl formate (**1a**) showed that the folded *sp*-conformer (**A**) is still the most stable and that the CH–π-interacted *ap*-conformer (**B**) is 0·91 kcal mol^{-1} less stable than **A**. The CH–π interaction forces it to take the *ap*-ester structure, which is considered to be disadvantageous[14,20] because of unfavourable intramolecular dipole–dipole interaction between carbonyl and alkoxyl groups. For this reason, on starting this study we expected that the extended conformer (**C**) should be predominant over the CH–π-interacted conformer. The LIS experiments, however, showed that the *AF* value for the CH–π contiguous *ap*-conformer (**B**) is the lowest in some cases and as low as for the extended conformer **C** with all three series of compounds **1**, **2** and **3**. The difference in the *AF* values between the folded *ap*-conformer (**B**) and the extended *sp*-conformer (**C**) is generally small. This suggests the coexistence of comparable amounts of the two conformers in equilibrium. The C=O–π contiguous folded *sp*-conformation (**A**) seemed improbable from the LIS experiments.

In order to obtain further information concerning the conformations of the formate esters **1**–**3**, ^{1}H NOE difference spectra were measured. Here, the NOE enhancement of H_x induced by the irradiation of the *S* signal will be denoted as $f_{H_x}(S)$. The results are given in Table 4 and the calculated interatomic distances d_{ij} between various hydrogen atoms in the conformers **A**–**D** of *p*-methoxybenzyl formate (**1b**) are given in Table 5.

NOE enhancement of the proton signals tends to

Table 4. Difference ^{1}H NOE data [enhancement $f_{H_x}(S)$ in %] of benzyl, 1-phenylethyl and cumyl formates (**1**, **2** and **3**) with $CDCl_3$ as solvent unless stated otherwise[a]

	Substituted Benzyl Formates									
	1b (X = *p*-MeO)		**1c** (X = *p*-Me)		**1a** (X = H)[b]		**1d** (X = *p*-Cl)		**1e** (X = *p*-NO$_2$)	
Observed nucleus	H_{Ar}	H_{CHO}	H_{Ar}	H_{CHO}	H_{Ar}	H_{CHO}	H_{Ar}	H_{CHO}	H_{Ar}	H_{CHO}
Irradiated nucleus: H_α	3·7 (6·3, 1·1)	0·8	2·5	0·8	2·8	0·8	2·2	0·6	3·0 (4·4, 1·6)	0·4
Observed nucleus	H_{Ar}	H_α	H_{Ar}	H_α	H_{Ar}	H_α	H_{Ar}	H_α	H_{Ar}	H_α
Irradiated nucleus: H_{CHO}	4·2 (5·2, 3·2)	1·8	3·4	1·9	3·0	1·9	2·8	1·9	2·4 (3·2, 1·6)	1·9
In DMSO-d_6	5·1 (5·7, 4·4)	1·7	4·1	2·2	3·6	2·2	3·3	2·1	—	—
In C_6D_6	3·4 (4·1, 2·8)	1·7	2·3	1·5	2·0	1·6	1·7	0·9	—	—

	Substituted 1-phenylethyl and cumyl formates										
	2b (X = *p*-Me)			**2a** (X = H)			**2c** (X = *p*-Cl)			3 (X = H, cumyl)	
Observed nucleus	H_{Ar}	H_{CHO}	$H_{\alpha\text{-Me}}$	H_{Ar}	H_{CHO}	$H_{\alpha\text{-Me}}$	H_{Ar}	H_{CHO}	$H_{\alpha\text{-Me}}$		
Irradiated nucleus: H_α	4·8	0·6	3·7	4·8	1·5	5·7	4·0	0·9	4·3	—	—
Observed nucleus	H_{Ar}	H_α	$H_{\alpha\text{-Me}}$	H_{Ar}	H_α	$H_{\alpha\text{-Me}}$	H_{Ar}	H_α	$H_{\alpha\text{-Me}}$	H_{Ar}	$H_{\alpha\text{-Me}}$
Irradiated nucleus: H_{CHO}	4·2	1·0	2·7	3·8	1·3	2·2	3·2	1·5	1·7	3·0	1·9
In DMSO-d_6	5·5	2·2	3·2	4·9	2·8	3·7	3·7	2·5	2·8	—	—
In C_6D_6	2·8	0·7	2·1	2·4	0·9	1·9	2·1	0·8	1·3	—	—
Observed nucleus	H_{Ar}	H_α	H_{CHO}	H_{Ar}	H_α	H_{CHO}	H_{Ar}	H_α	H_{CHO}	H_{Ar}	H_{CHO}
Irradiated nucleus: $H_{\alpha\text{-Me}}$	1·5	2·5	0·6	1·5	2·1	0·4	1·3	2·0	0·3	2·2	0·6

[a] In the cases of **1b** and **1e**, the enhancements of *ortho*- and *meta*-protons can be observed separately. The enhancements for *o*-H and *m*-H are given in this order in parentheses.

[b] NOE enhancements $f_{H_o}(H_\alpha) = 2·5$, $f_{H_m}(H_\alpha) = 0·7$, $f_{H_o}(H_{CHO}) = 2·3$ and $f_{H_m}(H_{CHO}) = 1·3$ were obtained by separating the *ortho*- and *meta*-proton signals by adding a shift reagent.

Table 5. Interatomic distances d_{ij} (Å) in *p*-methoxybenzyl formate (**1a**)[a] computed from the optimized geometries by PM3 calculations

		A (0)[b]	**B** (0·845)[b]	**B′**	**C** (0·891)[b]	**D** (2·99)[b]
H_{CHO}—H_α	Min.	3·67	2·61	3·35	3·68	3·67
	Max.	3·94	3·65		3·69	3·94
H_{CHO}—H_o	Min.	4·59	3·05	3·16	4·95	4·59
	Max.	4·83	4·26		4·96	4·83
H_{CHO}—H_m	Min.	6·42	4·80	4·32	6·95	6·42
	Max.	6·59	5·65		6·96	6·60
H_α—H_o	Min.	2·43	2·36	2·50	2·47	2·43
	Max.	3·74	3·78	3·73	3·72	3·74
H_α—H_m	Min.	4·71	4·69	4·76	4·74	4·71
	Max.	5·47	5·54	5·50	5·51	5·52

[a] The *p*-methoxy derivative is the most suitable for the analysis because the ^1H signals of aromatic protons can be observed separately.

[b] Relative energy (kcal mol^{-1}).

decrease very sharply as the distance (d_{ij}) between the irradiated (i) and the observed (j) protons increases, since it is a very short-range effect proportional to d_{ij}^{-6}. Hence NOE can usually be observed only when the interatomic distance is less than 5 Å. For this reason, NOE between aromatic and formyl protons must be useful to show critically the presence of the folded *ap*-conformer (**B**) of **1**. In the extended conformers (**C** and **D**) and the folded *sp*-conformer (**A**), the H_{CHO}—H_{Ar} distance is 4·59 Å at the shortest and the H_{Ar} are too far to be enhanced considerably by the irradiation on H_{CHO}. In the cases of **1b** (X = OCH_3) and **1e** (X = NO_2), the intensities of *ortho*- and *meta*-protons could be measured separately, giving their individual enhancement values. As the calculated H_{CHO}—H_m distances are more than 6 Å except for the folded *ap*-conformer (**B**) capable of a CH–π interaction, the presence of this conformer can be verified by the fact that the enhancement of the *meta*-hydrogen signal was observed by the irradiation of the formyl signal. The enhancement of the *meta*-hydrogen signal [$f_{H_m}(H_{CHO})$] is 70% of the *ortho*-hydrogen signal [$f_{H_o}(H_{CHO})$] in the case of *p*-methoxybenzyl formate (**1b**), which can only be accounted for by assuming the predominance of the CH–π contiguous *ap*-conformer (**B**).

However, the enhancement of the aromatic proton signals [$f_{H_o}(H_{CHO})$ and $f_{H_m}(H_{CHO})$] were larger than expected from the H_{CHO}—H_o and H_{CHO}—H_m interatomic distances calculated from the PM3-optimized geometry of **B**. This suggested that the distances between the formyl and the aromatic protons are closer than calculated. We therefore tried to search for the conformation best fitted for the observed NOE by rotating the formyl group about the O—C_α bond while keeping the *ap*-conformation of the formate ester moiety. In practice, the C_{CHO}—O—C_α—C_{ipso} torsional angle (ω_1) was driven from −70° to 0° around the PM3-optimized value ($\omega_1 = -50°$) of conformer **B** at intervals of 5° and the conformation giving the least square error was searched for. Surprisingly, the Ar/formyl *cis ap*-conformation (**B′**, $\omega_1 = 0°$) which is symmetrical about the plane bisecting the aromatic ring, was shown to be best fitted with the observed NOE (Figure 2). The $f_{H_{arom}}(H_\alpha)$ and $f_{H_{formyl}}(H_\alpha)$ values are in accord with this conformation. This conformation (**B′**) is also located in the wide low-*ΔF* plateau area in Figure 1 and is in accord with the LIS experiments. [The NOE measurements on LSR-added solutions of some formates suggested that the complex formation with LSR disfavours the CH–π-interacted conformer **B** (or **B′**). Thus, $f_{H_{Ar}}(H_{CHO})$ of **1b** became as low as 3·6% (4·6% and 2·6% for H_o and H_m, respectively), when a 0·15 mol ratio of $Eu(fod)_3$ was added to the chloroform solution. In contrast, $f_{H_\alpha}(H_{CHO})$ remained almost constant after the addition of the LSR.]

The formyl hydrogen is located closest to the aromatic ring in conformation **B′**. In this conformation, the formyl C—H bond orients itself nearly perpendicular to the aromatic ring (hence θ in Figure 2 is the smallest). These geometric features of the conformation **B′** surely favour the formation of CH–π interactions. As the conformer **B** was estimated to be the second most stable from the PM3 calculation, its unexpected predominance can only be rationalized by taking into account the stabilization by CH–π interactions. Our

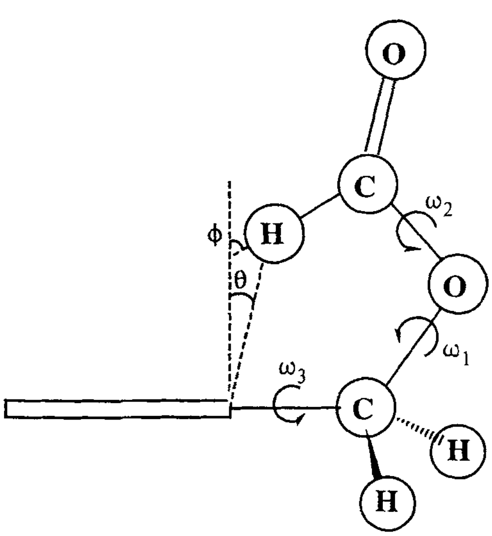

Figure 2. The most probable conformation (**B′**) from NOE data. The CH–π interaction becomes most favourable when a C—H bond approaches from perpendicular to the aromatic ring ($\omega_3 = 90°$, $\theta = 0°$). The angle φ is smallest in this conformation, and the overlap between the aromatic π-orbital and the C—H antibonding σ*-orbital becomes maximum

previous experiments on intermolecular CH–π interactions showed that the enthalpy of formation is *ca* 2 kcal mol^{-1} for the CH–π complexes of benzene with chloroform and trichloroacetaldehyde.[21] Therefore, the intramolecular CH–π interaction between the formyl CH and the aromatic π-electrons can reverse the order of the conformational energies and contribute to stabilizing the distorted folded *ap*-conformer (**B**′).

However, our experiments by no means exclude the presence of considerable amounts of other conformers. In the series of benzyl formates (**1a**–**1e**), the NOE enhancements of $[f_{H_{arom}}(H_{CHO})]$ are regularly dependent on the electronic properties of *para*-substituents in contrast to those of benzyl protons $[f_{H_\alpha}(H_{CHO})]$. This can be best explained by assuming that conformer **B** is in equilibrium with another conformer, presumably an extended one (**C**). The $f_{H_{arom}}(H_{CHO})/f_{H_\alpha}(H_{CHO})$ ratio increases as the substituent becomes more electron donating, suggesting that the CH–π contiguous conformer **B**′ should become more favourable in this order. This can be additional evidence for the hydrogen bond-like nature of the formyl CH–aromatic π-electron interaction. A formyl hydrogen is rather a strong CH acid, which enabled us to establish the hydrogen bond-like substituent effect clearly. A similar trend of substituent effects was observed with substituted 1-phenylethyl formates (**2**), although the number of substituted analogues examined is obviously too small to draw conclusions on the trend without a comparison with the results for the benzyl formates **1a**–**e**.

Our previous investigations on the intramolecular CH–π interactions of substituted 1-phenylethyl isopropyl ketones and 1-phenylethyl alkyl ethers, and on the intermolecular CH–π interaction of chloroform with several aromatic π-bases, had revealed similar trends in the substituent effects that were interpreted in terms of hydrogen bond-like interactions. The present findings add support on our view that the interaction should be a sort of hydrogen bonding of the weakest limit.

EXPERIMENTAL

Materials. Substituted benzyl and 1-phenylethyl formates were prepared by reaction of the corresponding benzyl alcohols with *N*-formylimidazole in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene. The formylating reagent was prepared from *N,N*-carbonyldiimidazole and formic acid. The raw formates were distilled *in vacuo* and chromatographed on silica gel when necessary. Boiling points: **1b**, 53·8–54·3 °C (2·0 mmHg); **1c**, 93·0–94·0 °C (5·0 mmHg); **2a**, 42·0–43·0 °C (1·5 mmHg); **2b** 59·0–59·5 °C (5·0 mmHg); **2c**, 50·5–51·3 °C (0·5 mmHg); **3**, 55·5–56·3 °C (1·0 mmHg).

Commercially available Eu(fod)$_3$ was purified by sublimation before use.

Measurements. NOE difference spectra were obtained on a JEOL-EX-270 NMR spectrometer at 30 °C. The NOE enhancements were recorded at three different irradiation power, and their averages are given in Table 3.

^{1}H and ^{13}C lanthanoid-induced shift (LIS) measurements were carried out on chloroformed-*d* solutions containing *ca* 0·2 mol l^{-1} of the substrate (a formate) using Eu(fod)$_3$ as the lanthanoid shift reagent (LSR). The LSR was added successively in five equal portions to the solution; each addition was followed by an NMR measurement. The LIS was obtained from the gradient of a plot of the chemical shift *vs* the concentration of added Eu(fod)$_3$. The final concentration of the shift reagent was kept lower than 0·2 mol equivalent of the substrate so as to obtain a linear LIS vs concentration plot. The plots were exactly linear in this region, giving correlation coefficients higher than 0·99 except for the ^{13}C LIS of *p*-nitrobenzyl formate (**1d**).

Calculations. The LIS for each nucleus was calculated by assuming the location of the lanthanoid ion (Eu^{3+}) and by using the McConnell–Robertson equation [equation (2)]. The C=O—Eu angle was fixed at 130° throughout the calculation and the O—Eu distance was altered from 3·0 to 4·0 Å at intervals of 0·2 Å. The distance r_i and the angles χ_i were calculated with all stable conformations of the substrate molecules by MM2, which allowed us to compute the LIS$_{calc}$ values.

Molecular mechanics and molecular orbital calculations were performed by use of MM2[22] and PM3[19] programs, respectively.

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