Journal of Organometallic Chemistry, 108 (1976) 371—380
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THE INTERNAL ROTATION OF ACYL GROUPS IN ACYLFERROCENES. A ^{1}H AND ^{13}C DNMR STUDY

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(Received October 30th, 1975)

Summary

The barriers to acyl group rotation in a series of acylferrocenes, including 1,1'-diacetylferrocene, have been determined by ^{1}H and ^{13}C DNMR. Complete lineshape analysis over wide temperature ranges gave $\Delta G^{\neq}_{173}$ 8.79 ± 0.03 kcal mol^{-1}, $\Delta H^{\neq}$ 7.5 ± 0.3 kcal mol^{-1} and $\Delta S^{\neq}$ —8 ± 2 cal mol^{-1} K^{-1} for [^{2}H]formylferrocene and $\Delta G^{\neq}_{173}$ 8.51 ± 0.02 kcal mol^{-1}, $\Delta H^{\neq}$ 7.1 ± 0.2 kcal mol^{-1} and $\Delta S^{\neq}$ —8 ± 2 cal mol^{-1} K^{-1} for acetylferrocene. The unexpectedly high barrier in diferrocenylketone ($\Delta G^{\neq}_{143}$ 6.8 ± 0.2 kcal mol^{-1}) is interpreted in terms of strain in the transition state, and the relatively low barrier in 1,1'-diacetylferrocene ($\Delta G^{\neq}_{163}$ 7.8 ± 0.3 kcal mol^{-1}) is ascribed to an interannular effect.

Introduction

The π-electron interaction between an aromatic or heteroaromatic ring and an acyl group is manifested by a twofold barrier to rotation of the acyl group. Following the pioneering work of Anet and Ahmad [1] and of Dahlqvist and Forsén [2], barriers to acyl rotation have been measured in a great number of aromatic and heteroaromatic systems, mostly using the ^{1}H dynamic NMR (DNMR) technique [3—9] but more recently also the often more powerful ^{13}C DNMR technique [10,11].

The effect of *para*-substituents in aromatic aldehydes and ketones [1,3,10] and a comparison of the free energy barriers to *E—Z* rotation in furanaldehyde (10.3 kcal mol^{-1} [2]) and 1-methyl-2-pyrrolaldehyde (12.5 kcal mol^{-1} [5]) indicate, in agreement with ground-state expectations, that the barrier increases with increasing electron-donating capacity of the ring. This picture has been corroborated by a quantitative analysis of the interaction of donor and acceptor groups through benzene rings, using rotational barriers [9].

Since the ferrocenyl group is one of the most powerful electron-releasing

TABLE 1

^{1}H NMR SPECTRAL PARAMETERS FOR ACYLFERROCENES (FcCOR) IN $CHCl_2F$ AT 30°C

Compound	$\delta(2,5)^a$	$\delta(3,4)$	$\delta(C_5H_5)$	$\delta(R)$	J_{23} (Hz)	J_{24} (Hz)	J_{25} (Hz)	J_{34} (Hz)	J_{R2} (Hz)	J_{R3} (Hz)
FcCDO	4.768	4.578	4.246							
FcCHO	4.757 ^{b}	4.568 ^{b}	4.243	9.917					0.3	0.5
$FcCOCH_3$	4.745	4.468	4.173	2.338	2.58	1.26	1.28	2.42		
FcCOPh	4.881 ^{b}	4.561 ^{b}	4.174							
Fc_2CO	4.979 ^{b}	4.502 ^{b}	4.177							
1,1′-Diacetylferrocene	4.748 ^{b}	4.475 ^{b}		2.310						

[a] In ppm downfield from TMS. [b] Middle of triplet.

aromatic groups, we have found it of interest to study the rotational barriers in ferrocenaldehyde, acetylferrocene, benzoylferrocene, and diferrocenylketone by ^1H and ^{13}C DNMR technique. In order to study the interannular interaction [12,13], 1,1′-diacetylferrocene was also included. To simplify the spectrum, the ^1H study of ferrocenaldehyde was performed on the [^2H] formyl derivative.

Experimental

Synthetic part. Ferrocenaldehyde (FcCHO) [14], acetylferrocene ($FcCOCH_3$) [15], benzoylferrocene (FcCOPh) [16], diferrocenylketone (Fc_2Co) [17], and 1,1′-diacetylferrocene [18] were prepared by literature methods. Ferrocene-[^2H]aldehyde (FcCDO) was prepared by reduction of methyl ferrocenemonocarboxylate with lithium aluminium deuteride (70% yield), followed by oxidation of the [$^2H_2$]ferrocenylcarbinol with "active" manganese dioxide [19] in chloroform to give the desired compound in 65% yield. The identity and isotopic purity of the labelled aldehyde (after purification via the bisulphite addition compound) and of the intermediate carbinol were checked by GLC and by infrared, NMR and mass spectra.

NMR spectra. The ^1H spectra were recorded on a JEOL Model JNM-MH-100 NMR spectrometer, equipped with a standard variable temperature attachment (VT 3-c), and operating in the internal lock mode with TMS as the lock signal. The chemical shifts were measured by a Hewlett—Packard Model 3734A frequency counter. The spectra were recorded at a sweep rate of 0.216 Hz sec^{-1}, and the radio frequency field was kept well below the saturation level.

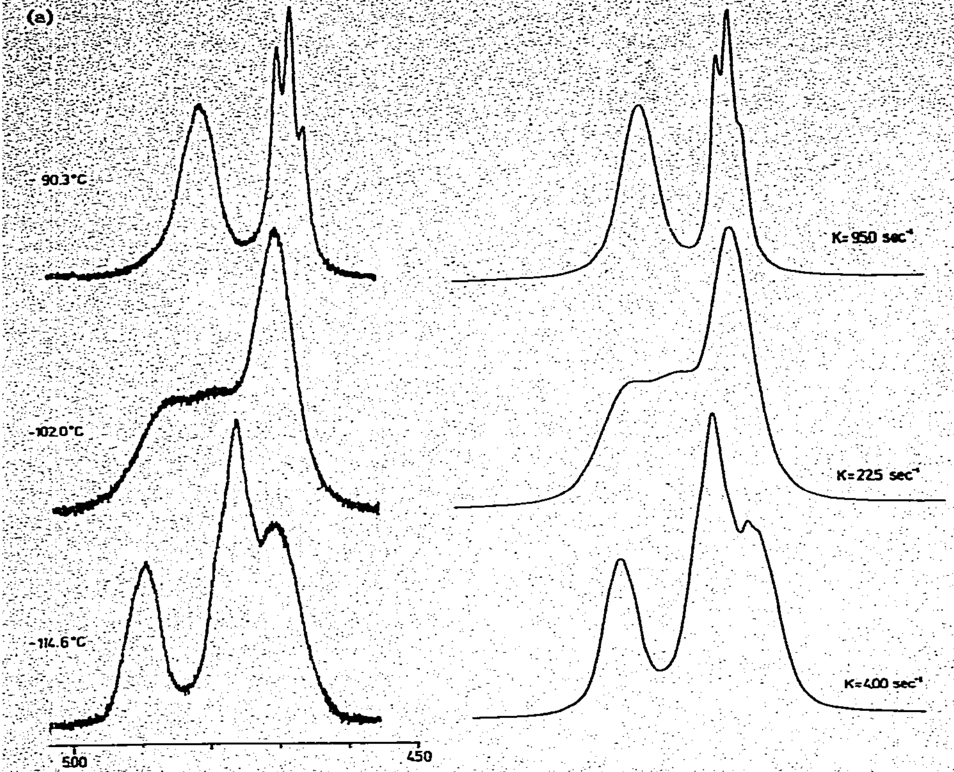
The ^{13}C spectra were recorded on a JEOL Model FX 60 FT NMR spectrometer equipped with an NM-5471 temperature controller and an NM-5490 variable temperature adapter. Some spectra were also recorded on a VARIAN Model XL-100-15 NMR spectrometer equipped with a V-6040 temperature controller and a Model VFT-100-X Fourier transform system.

The solvent for the ^1H spectra was dichlorofluoromethane, and for the ^{13}C spectra the same solvent with 20% (v/v) of [^2H]$_6$acetone to provide a lock signal. The concentration was 0.5 *M* except for diferrocenylketone and 1,1′-diacetylferrocene, which could only be obtained as 0.15 *M* solutions. TMS was added to serve as an internal reference and to provide the ^1H lock signal. The samples were degassed by several freeze—thaw cycles under high vacuum, before being sealed off.

The temperatures were measured as described previously [20]. In the case of the ^{13}C spectra, calibration was made under the same decoupling conditions as when the spectra were recorded. Due to the long recording times, the temperatures for the ^{13}C spectra are accurate only to ±1°C, whereas the temperatures for the ^1H spectra in most cases varied over less than 0.6°C.

Evaluation of rate constants and thermodynamic parameters

(a) ^1H spectra. Analysis of the ^1H spectra of FcCDO and $FcCOCH_3$ at ambient temperature was performed by the program UEAITR/Flex 8 [21], and the resulting spectral parameters are found in Table 1. The assignments are based on those of Rausch and Siegel [22]. Due to a small residual coupling to the ^2H atom, the analysis of the FcCDO spectrum did not give an entirely



reliable result. However, calculation of the spectrum using the coupling constants derived for $FcCOCH_3$ gave very good agreement, and these were used in the lineshape calculations for both compounds. Due to the low barriers, no resolved spectra could be obtained in the slow exhange limit, and J_{24} and J_{35} had to be given the same time-average value, though these couplings may well be slightly different when the acyl group rotation is slow.

The rate constants for FcCDO and $FcCOCH_3$ were evaluated by visual comparison between experimental spectra and spectra calculated by the program DNMR3 [23] for an ABCD $\rightleftharpoons$ BADC exchange (Fig. 1). A non-negligible temperature dependence of the time-average chemical shifts was observed in the fast exchange limit, and the shifts for the exchange broadened spectra were obtained by adjustment at low exchange rates and extrapolation to regions of higher exchange rates. T_2 values were determined from the linewidth of the signal of the unsubstituted ring.

The rate constants (k) for the internal rotation in FcCDO were determined at 17 temperatures in the range 158 to 189 K, and from the slope and intercept of the least squares plot of $\ln(kT^{-1})$ vs. T^{-1} (Fig. 2), $\Delta H^{\neq}$ and $\Delta S^{\neq}$ could be calculated. Similarly, $FcCOCH_3$ was studied at 19 different temperatures in the range 155 to 183 K. The results are found in Table 2.

By using the simple coalescence expression 1 * on the 2- and 5-proton signals,

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* Derived from the expression for a coalescing doublet [24] in conjunction with the Eyring equation [25].

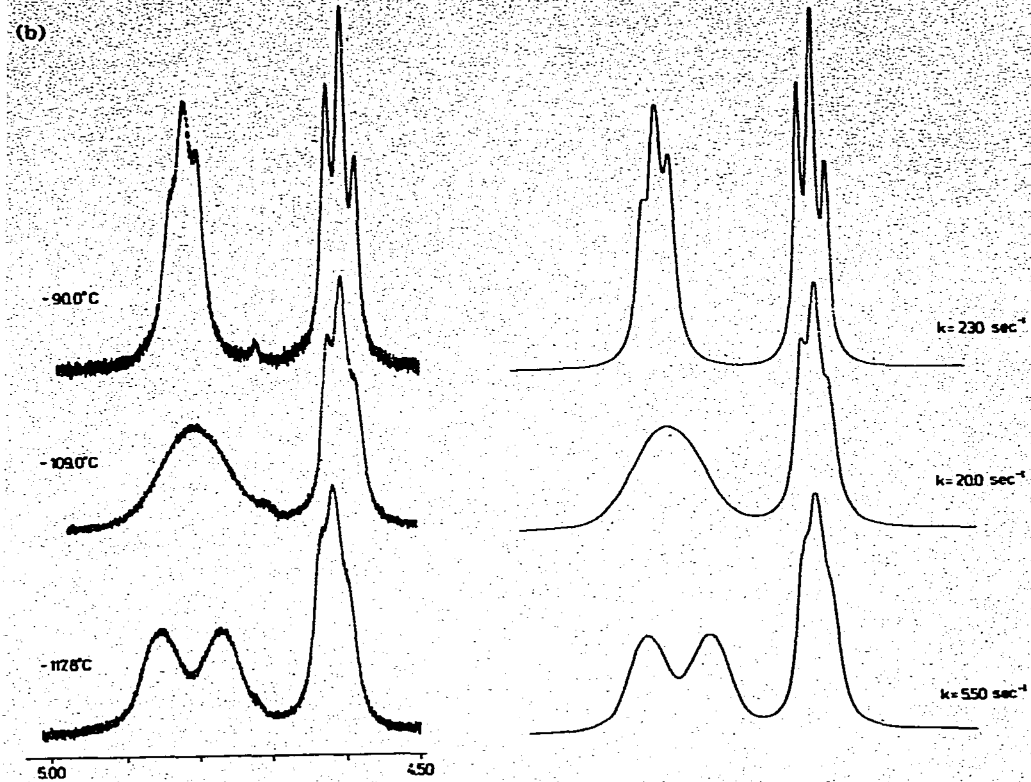

Fig. 1. Experimental and theoretical ^1H NMR spectra of FcCDO (a) and $FcCOCH_3$ (b).

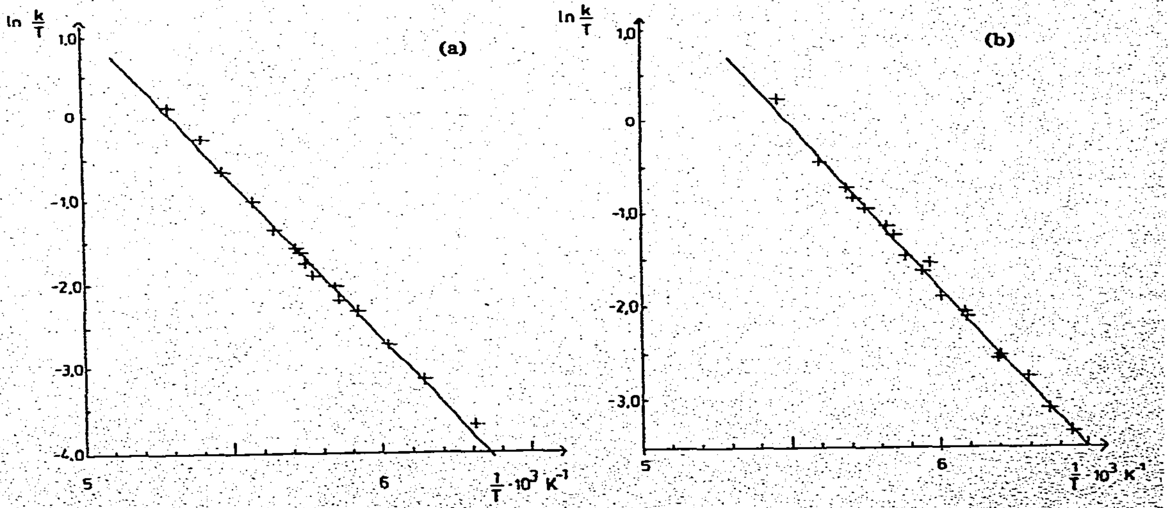

Fig. 2. Plot of ln(kT^{-1}) vs. T^{-1} for FcCDO (a) and $FcCOCH_3$ (b).

TABLE 2

THERMODYNAMIC PARAMETERS FOR THE ACYL ROTATION IN FcCOR (in S.I. units in parentheses)

R	$\Delta G^{\neq}_{173}$ (kcal mol^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal mol^{-1} K^{-1})
D	8.79 ± 0.03 [a]	7.5 ± 0.3	−7.7 ± 1.8
	(36.8 ± 0.1)	(31.2 ± 1.3)	(−32.2 ± 7.5)
CH_3	8.51 ± 0.02	7.1 ± 0.2	−8.4 ± 1.5
	(35.6 ± 0.1)	(29.7 ± 0.8)	(35.1 ± 6.3)

[a] Calculated at the 95% confidence level, assuming only random errors.

and for FcCDO also the 3- and 4-proton signals, approximate free energy

$$\Delta G^{\neq}_{T_c} = 0.004573\, T_c\, (9.972 + \log T_c - \log \Delta\nu_0) \qquad (1)$$

barriers could be calculated. Since the values thus obtained (Table 3) deviated by no more than 0.1 kcal mol^{-1} from those obtained by the complete lineshape analysis, it was regarded as permissible to use expression 1 also for FcCOPh and Fc_2CO, for which the coalescence could be observed but no resolved low-temperature spectra could be obtained. The values obtained are found in Table 3. This technique could not be used with 1,1′-diacetylferrocenes since no splitting was observed in the ^{1}H spectrum down to −140°C. As is shown by the ^{13}C spectra (vide infra) this is due to an accidental overlap of the 2- and 5-proton signals rather than to a low barrier.

(b) ^{13}C spectra. The ^{13}C spectra of a large number of ferrocene derivatives, including FcCHO, $FcCOCH_3$, and FcCOPh, have been studied in deuteriochloroform solution by Nesmeyanov et al., [26] and our results are quite similar in spite of the difference in solvent (Table 4). At ambient temperature the C_2, C_5 signal in the FcCHO spectrum coincides with the signal of the carbon atoms in the unsubstituted ring, and in the $FcCOCH_3$ spectrum the difference is only 0.3 ppm. Consequently, at lower temperatures the signal from the unsubstituted ring falls between the C_2 and C_5 signals, which complicates the lineshape analysis. The rate constants for acyl rotation in FcCHO and $FcCOCH_3$ were determined by visual fitting of the experimental spectra to curves calculated by superposition of the spectra of two exchanging doublets [27] (C_2—C_5 and C_3—C_4). The results (Table 5) agree well with those obtained from ^{1}H spectra

TABLE 3

FREE ENERGY BARRIERS OBTAINED FROM ^{1}H COALESCENCE DATA

Compound	$\Delta\nu$(Hz)	T_c(K)	$\Delta G^{\neq}_{T_c}$ (kcal mol^{-1})
FcCHO	12.2 [a]	173	8.8 ± 0.2
	5.6 [b]	168	8.8 ± 0.2
$FcCOCH_3$	7.9 [a]	163	8.4 ± 0.2
FcCOPh	40 [a]	144	6.9 ± 0.2
Fc_2CO	37 [a]	143	6.9 ± 0.2

[a] $|\nu_2 - \nu_5|$. [b] $|\nu_3 - \nu_4|$.

TABLE 4

^{13}C NMR CHEMICAL SHIFTS [a] FOR ACYLFERROCENES IN $CHCl_2F$ WITH 20% $(CD_3)_2CO$ AT 30°C

Compound	δ(1)	δ(2,5)	δ(3,4)	δ(α)	δ(unsubst.)	δ(CH_3)
FcCHO	80.4	70.1	76.3	193.6	70.1	
$FcCOCH_3$	80.1	70.1	72.8	202.0	70.4	27.4
FcCOPh	79.0	72.0	73.1	199.3	70.7	
1,1-Diacetylferrocene	81.7	71.6	74.1	201.2		27.7

[a] In ppm downfield from TMS.

TABLE 5

RATE CONSTANTS AND FREE ENERGY BARRIERS IN ACYLFERROCENES DERIVED FROM ^{13}C NMR SPECTRA

Compound	Δν (Hz)	T (K)	k (sec^{-1})	$\Delta G^{\neq}$ (kcal mol^{-1})
FcCHO [a]	103.8 [b]	179	67	8.80
	7.4 [c]	177	50	8.80
		173	28.6	8.78
		169	18.2	8.78
$FcCOCH_3$ [a]	57.0 [b]	199	1670	8.54
	7.0 [c]	186	333	8.56
		184	290	8.52
		179	200	8.41
		166	25	8.46
FcCOPh [d]	186 [b]	151	413	6.8 ± 0.2
1,1′-Diacetylferrocene [d]	53 [b]	163	117	7.8 ± 0.2

[a] By complete lineshape analysis. [b] $|\nu_2 - \nu_5|$. [c] $|\nu_3 - \nu_4|$. [d] By the coalescence approximation.

except for the values at the lowest temperatures. The deviations may be due to an extra broadening caused by overlap with the signal from the unsubstituted ring. The error introduced by this effect becomes progressively more serious as the exchange broadening diminishes. The free energy barriers for FcCOPh and 1,1′-diacetylferrocene were determined by the coalescence approximation 1 applied to the C_2 and C_5 signals (Table 5), wheras Fc_2CO was too insoluble in the solvent used to give a resolved low temperature spectrum.

The exchange broadened ^{13}C spectra of FcCHO and $FcCOCH_3$ were calculated on a Hewlett—Packard Model 9820A calculator and plotted on a Model 9862A plotter from the same company.

Discussion

(a) Comparison of the barriers in FcCHO and $FcCOCH_3$ with those in the benzene analogs

By measuring the basicity of $FcCOCH_3$ and correlating it with those of substituted acetophenones, Arnett and Bushick [28] derived a σ^+ value of 1.54 for the ferrocenyl group on a scale where σ^+ for phenyl is zero, for *p*-anisyl —0.7 and for *p*-dimethylaminophenyl —1.7 [29]. A similar comparison of the basicity of

Fc_2CO with that of a series of benzophenones gave σ^+ —1.09. Drakenberg et al. [10] found a good linear correlation between the free energies of activation and the σ^+ values for *para* substituents in a series of benzaldehydes. Using their $\Delta G^{\neq}$ values and assuming the same $\Delta S^{\neq}$ value for all compounds, a ρ value of +1.89 ± 0.17 for the aldehyde group rotation at 173 K can be deduced. The $\Delta S^{\neq}$ value for the benzaldehydes was taken to be 1.7 cal mol^{-1} K^{-1} as determined by a complete lineshape study of *p*-dimethylaminobenzaldehyde in a 1:1 mixture of dichlorofluoromethane and chlorodifluoromethane [10], (cf. the value of 2.5 cal mol^{-1} K^{-1} in dichloromethane [9]). This ρ value together with the σ^+ value from $FcCOCH_3$ gives an expected $\Delta G^{\neq}_{173}$ value of 9.9 ± 0.2 kcal mol^{-1} for FcCHO, notably higher than the observed value of 8.8 kcal mol^{-1}.

This analysis shows that the capacity of the ferrocenyl group to promote oxygen protonation in $FcCOCH_3$ is distinctly higher than its capacity to impede rotation in FcCHO. The difference may have several causes. One is the carbenium ion character of the protonated $FcCOCH_3$, which may lead to stabilization through interaction of iron orbitals with the C_α atom, frequently discussed for ferrocenylcarbonium ions [30]. It is also possible that the transition state to rotation of the acyl group is stabilized by an interaction between an oxygen lone pair and an empty iron 4*p* orbital. In that case, the rotation should have one preferred pathway, which will decrease the entropy of activation by 1.4 cal mol^{-1} K^{-1} besides lowering the $\Delta H^{\neq}$ value. However, this effect is not sufficient to explain the low activation entropies in FcCHO and $FcCOCH_3$ compared with those in the aromatic aldehydes. It is possible that changes in solvation and/or in inter-ring rotation [31] may be involved, but at present no satisfactory model for treating these effects is available.

The small barrier difference between FcCHO and $FcCOCH_3$, 0.4 kcal mol^{-1} in $\Delta H^{\neq}$, is also of some interest. As can be seen in Table 6, the barrier difference between the formyl and acetyl derivatives in the benzene series is considerably larger, 1.6—2.8 kcal mol^{-1}. This difference is mainly steric in origin [34], and in the case of dimethylamino compounds the initial state strain in the acetyl derivative is probably increased by the higher twofold torsional barrier, leading to a lower observed barrier and a large barrier difference. As can be expected, this difference is smaller in the five-membered heterocyclic analogs (0.8—1.4 kcal mol^{-1}), and the value for the ferrocene analogs, while still smaller, fits well into this picture.

(b) *Comparison of the barriers in FcCOPh and Fc_2CO*

The barriers calculated for these compounds from the observed rate constants at coalescence are both 6.9 kcal mol^{-1}. However, for strict comparability the rate constant for Fc_2CO should be divided by two, since the probability of a ferrocene group rotation is twice as large in Fc_2CO as in FcCOPh, other things being equal. This gives a $\Delta G^{\neq}$ value of 7.1 kcal mol^{-1} for Fc_2CO, which is unexpectedly high. One should rather predict a lower $\Delta G^{\neq}$ value for Fc_2CO than for FcCOPh. The explanation may be found in strain in the transition state. Fc_2CO has a transoid structure [38], and if the transition state approaches the cisoid arrangement, extra steric strain may build up. Furthermore, the initial state steric strain must be larger in FcCOPh than in Fc_2CO, a factor which contributes to the observed effect.

TABLE 6

LITERATURE VALUES FOR ROTATIONAL BARRIERS IN AROMATIC AND HETEROAROMATIC C—FORMYL AND C—ACETYL COMPOUNDS

Compound	Phase	Method	$\Delta G^{\neq}/\Delta H^{\neq}/V_2$ (kcal mol^{-1})	Ref.
PhCHO	Gas	IR	4.92	32
	Gas	Microwave	4.90	33
	Gas	Emp. force-field	4.90	34
	Solution	^{1}H DNMR	7.9	1
	Solution	^{13}C DNMR	7.6	10
$PhCOCH_3$	Gas	IR	3.1	32
	Gas	Emp. force-field	3.14	34
	Solution	Estimated	6.3	35
	Solution	^{13}C DNMR	5.9	36
p-$(CH_3)_2NC_6H_4CHO$	Solution	^{13}C DNMR	11.2	10
p-$(CH_3)_2NC_6H_4COCH_3$	Solution	^{1}H DNMR	8.3	9
2-Furanaldehyde	Solution	^{1}H DNMR	10.3 [a]	2
2-Acetylfuran	Solution	^{1}H DNMR	8.9 [a]	4
1-t-Butyl-3-pyrrolaldehyde	Solution	^{1}H DNMR	10.2 [b]	37
1-t-Butyl-3-acetylpyrrole	Solution	^{1}H DNMR	9.4 [b]	37

[a] $E \rightarrow Z$. [b] Conformers not stated.

(c) *Interannular interaction in 1,1′-diacetylferrocene*

The question of interannular interaction in ferrocenes has not been conclusively settled. Rosenblum et al. [13] found the UV-visible spectrum of 1-*p*-nitrophenyl-1′-anisylferrocene to be a composite of those of 1-*p*-nitrophenyl- and 1-anisyl-ferrocene. It may be argued that broad UV bands are not ideally suited for measuring small conjugation effects, and furthermore both substituent groups are electron acceptors in relation to ferrocene. It is also known that introduction of a deactivating substituent in one ferrocene ring lowers the rate of electrophilic substitution in the other ring quite drastically [13]. This effect, however, is explained by the mechanism of the reaction, proceeding through initial attack of the electrophile on the iron atom, utilizing the ferrocene e_{2g} orbital, which has considerable lone pair character. The deactivating substituent is considered to operate mainly by decreasing the availability of the electrons in the e_{2g} orbital [13].

The rotational barrier of 1,1′-diacetylferrocene is lower than that of $FcCOCH_3$ by 0.7 kcal mol^{-1}, a difference well above the experimental error. This may be a true interannular effect, in which one acetyl group inductively diminishes the interaction of the other ring with its acetyl group.

Acknowledgement

We are grateful to the Swedish Natural Science Research Council and to the Royal Physiographic Society of Lund for financial support. We also thank Dr. T. Drakenberg for communicating his experimental results prior to publication.

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