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Intramolecular hydrogen bonds and conformations of ferrocenyl- and nonamethylferrocenylcarbinols

E.S. Shubina, L.M. Epstein, T.V. Timofeeva, Yu.T. Struchkov, A.Z. Kreindlin, S.S. Fadeeva and M.I. Rybinskaya

Nesmeyanov Institute of Organoelement Compounds of the Academy of Sciences of the USSR, Vavilov St., 28, Moscow B-334 (U.S.S.R.)

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Abstract

The character of intramolecular hydrogen bonds in ferrocenyl- and nonamethylferrocenylcarbinols has been determined from their IR spectra and on the basis of molecular mechanics calculations. The intramolecular hydrogen bonds of the OH · · · Fe type are formed when the steric requirements of the substituents at the carbinol carbon atom and Cp rings make the corresponding conformations energetically favourable. The correlation of proton-donating ability of the ferrocenyl- and nonamethylferrocenylcarbinols relative to the stability of intramolecular hydrogen bonds is discussed.

The character and stability of intermolecular hydrogen bonds in crystals of the series of nonamethylferrocenylcarbinols and their non-methylated analogues have been discussed previously [1]. Here we describe the influence of the substituents at the carbinol C atom and Cp ligands on the character and relative stability of the intramolecular hydrogen bonds in solutions of these compounds.

Although the nature of intramolecular hydrogen bonds in α-ferrocenylcarbinols has been described previously [2–6], many questions remain unanswered. It is well known that two possible coordination centers, (i) the π-electrons of the Cp-rings and, (ii) the lone electron pairs of the Fe atom, are in competition to form an intramolecular hydrogen bond with the OH group. The changes in the ν(OH) region of the IR spectrum are so small (30–70 cm^{-1}) that their interpretation can be ambiguous.

We tried to solve the problem by combining an IR-spectral study of a large number of ferrocenyl- and nonamethylferrocenylcarbinols with the conformational calculations which enable the energetically favourable molecular conformations to be found.

A method widely used in organic chemistry, the molecular mechanics method (MMM), [7,8] was used for the conformational calculations. The application of

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Table 1

IR spectral data for ^{9}FcCHROH (I) and FcCHROH (II) in the ν(OH) region in CCl_4 and cyclohexane, the formation constants (K_f) for the intramolecular hydrogen bonds in CCl_4

R	^{9}FcCHROH					FcCHROH				
	CCl_4		cyclyhexane		Assign-	CCl_4		cyclohexane		Assign-
	ν	K_f	ν	Δν		ν	K_f	ν	Δν	
H (a)	3620	0			ν(free OH)	3620		3627		ν(free OH)
						3580	1.2	3585	42	ν(OH ··· π)
CH_3 (b)	3619		3623		ν(free OH)	3620		3620		ν(free OH)
	3590	7.0	3596	27	ν(OH ··· Fe)	3578	4.0	3589	31	ν(OH ··· π)
								3570	50	ν(OH ··· Fe)
C_6H_5 (c)	3613		3618		ν(free OH)	3612		3617		ν(free OH)
	3574	4.3	3578	40	ν(Fe ··· OH)	3570	3.2	3578	39	ν(OH ··· π)
						low		3550	67	ν(OH ··· Fe)
C_6F_5 (d)	3615		3618		ν(free OH)	3610		3615		ν(free OH)
	3590	3.0	3590	28	ν(OH ··· Fe)	3570	1.5	3570	45	ν(OH ··· π)
						low		3545	70	ν(OH ··· Fe)
Mes (e)	3615	0			ν(free OH)	3620		3620		ν(free OH)
						3570	0.3	3560	60	ν(OH ··· Fe)

Table 2

Spectral characteristics and enthalpies ($-\Delta H$(kcal/mol)) for the intermolecular hydrogen bonds of ^{9}FcCHROH and FcCHROH with DMSO

R	^{9}FcCHROH				FcCHROH			
	ν (cm^{-1}	$\Delta\nu$ (cm^{-1})	$\Delta\nu_{1/2}$	$-\Delta H$	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	$\Delta\nu_{1/2}$	$-\Delta H$
H (a)	3402	210	206	4.1	3390	230	216	4.4
CH_3 (b)	3416	201	190	3.9	3406	213	204	4.1
C_6H_5 (c)	3392	220	210	4.2	3373	244	222	4.6
C_6F_5 (d)	3340	270	258	4.9	3335	275	288	5.0
Mes (e)	3382	234	212	4.4	3378	236	220	4.4

MMM to conformational studies of organometallic molecules, although rare [9–12], are in fact, rather successful. Thus the application of this method in order to elucidate the steric features of the ferrocenylcarbinols under investigaiton is plausible. Our interest was directed at considering the different possible OHROH group orientations relative to the metallocene moiety. By MMM, the conformational energy (U_{conf}), a function of the torsion angle (ϕ) around the carbinol C–C bond, was calculated for molecules with substituents in the Cp ligand and at the carbinol C atom. The conformational analysis was carried out for ^{9}FcCHROH + (I) and FcCHROH * + (II) with R = H, CH_3, Mes, Bu^t.

Carbinols of types I and II with R = H (a), CH_3 (b), C_6H_5 (c), C_6F_5 (d), Mes (e), Bu^t (f) were chosen for the IR study. IR spectra were measured in CCl_4 and cyclohexane under conditions which precluded self-association (Table 1). Cyclohexane, a far more inert solvent than CCl_4, gave spectra with markedly narrowed bands in those cases in which the two ν(OH) bands, indicating the formation of intramolecular hydrogen bonds of two types present (as in [6] for IIc), could be discerned. Our spectral study was based on the fact that the OH band shift, $\Delta\nu$(OH) = ν(free OH) − ν(bonded OH) of cycles of the same size and the same H-bond partners could be regarded as a measure of the H-bond energy [13]. Spectra of carbionols in CCl_4/DMSO mixture as a standard proton-accepting solvent were measured for the estimation of proton-donating ability of the carbinols. The enthalpies of the intermolecular hydrogen bonds were evaluated by use of well-known equation:

$$-\Delta H = \frac{18\Delta\nu}{(\Delta\nu + 720)}\ [14]\ (\text{Table 2})$$

Results and discussion

The conformational calculations for primary ferrocenylcarbinol (IIa) and the related nonamethylderivative (Ia) do not reveal which regions correspond to the stable conformations. Substitution at the carbinol C atom leads to certain conformational differences in I and II, owing to increased steric hindrance.

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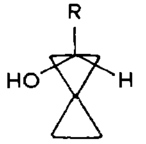
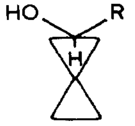
* ^{9}Fc = $C_5Me_5FeC_6Me_4$, Fc = $C_5H_5FeC_5H_4$.

There are three minima for U_{conf} when R = Me (IIb). They correspond to values of the ϕ angle by which the OH group rotated either towards the iron atom ($\phi = -100°$ (**1**)) or to above the Cp-ring ($\phi = +40°$ (**2**) and 140° (**3**)).



(**1**)



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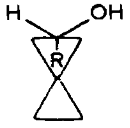

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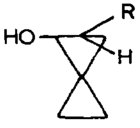

(**4**)

The differences in energy of the minima are less than 1 kcal/mol (Fig. 1), i.e. the steric factors do not cause prevalence of any one of the conformations and do not impose limitations on the formation of intramolecular hydrogen bonds with the Fe atom or Cp ligand. The limits imposed on the formation of the OH $\cdots$ π intramolecular hydrogen bond are imposed only by bulky substituents at the carbinol C atom, such as Mes in IIe or Bu^t in IIf. The conformational analysis for IIe gives three minima, the two lowest corresponding to the conformation with, (a) an almost coplanar position of the OH group and the Cp ring ($\phi \approx 0°$) (**4**), and (b) the OH group rotated towards the Fe atom ($\phi = -100°$) (**1**). In the first case the most favourable conformation (**4**), precludes the formation of intramolecular hydrogen bond. Introduction of a Bu^t substituent, which has even higher steric requirements leaves only one possible conformation, that of OH-group rotated towards the metal atom, viz. $\phi \approx -40°$(**1**), with a M $\cdots$ O distance of 3.2 Å. This conformation favours the formation of the OH $\cdots$ Fe intramolecular hydrogen bond. Conformations without intramolecular hydrogen bonds or with the OH group situated over the Cp ring are unrealistic because the rotation of the carbinol group to $\phi = 0°$ (corresponding to coplanarity of OH group and the ring) leads to an increase in U_{conf} by 14 kcal/mol.

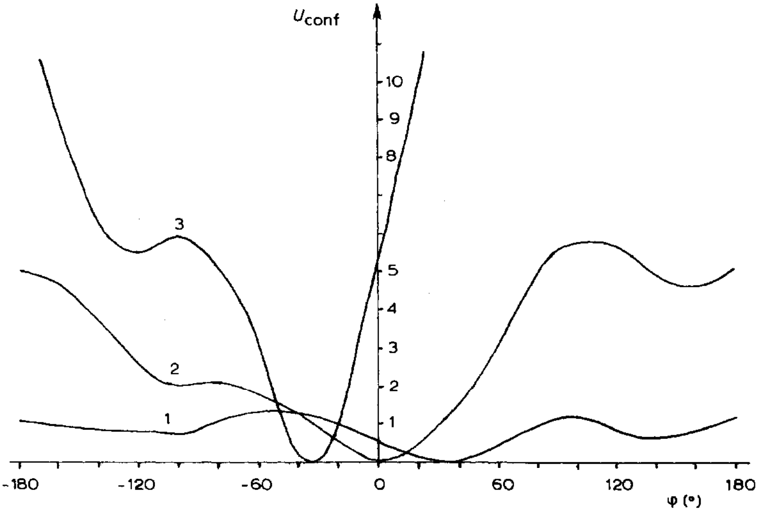

Fig. 1. The plot of U_{conf} (kcal/mol) vs. ϕ (angle of rotation around the C–C bond by carbinol group) in ferrocenylcarbinols: 1, R = Me (IIb); 2, R = Mes (IIe); 3, R = Bu^t (IIf).

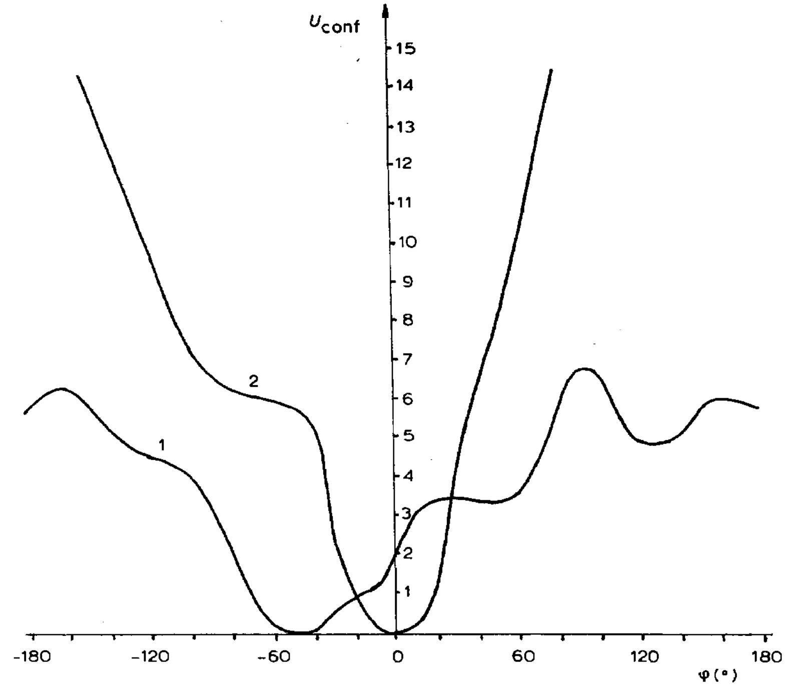

Fig. 2. The plot of U_{conf} (kcal/mol) vs. angle of rotation ϕ by carbinol group in nonamethylferrocenylcarbinols: 1, R = Me (Ib); 2, R = Mes (Ie).

The nine methyl substituents in the Cp ring cause considerable steric hindrance which make the position of the OH group over the ring unfavourable even in case of R = Me (Ib) (Fig. 2). The plot of U_{conf} vs. ϕ has three pronounced minima. The most stable conformation corresponds to $\phi = -50°$ (1) with an Fe · · · O distance of 3.5 Å which allows the formation of an intramolecular OH · · · Fe bond. A change in ϕ to $\phi \approx 40°$ (2), so as to correspond to the next conformational minimum, requires 3.5 kcal/mol. This means that the formation of an intramolecular OH · · · Fe bond is energetically favourable. Subsitution at the carbinol C atom with R = Mes, as in Ie, causes such steric crowding that the conformation, one of OH group near coplanarity with the ring ($\phi \approx 0°$, M · · · O 3.85 Å), proves to be the only one sterically possible, and the intramolecular hydrogen bond cannot be formed (**4**). This result is consistent with the X-ray diffraction data which indicate that there is such a conformation in crystals of Ie [1].

Thus conformational analysis shows that methylation of the Cp-rings in ferrocenylcarbinols reduces the number of energetically favourable conformations, which limits participation by Cp-ring π-electrons in the intramolecular H bond. Methylation also causes considerable steric hindrance thus preventing the rotation of carbinol group into an orientation suitable for OH · · · Fe bond formation, thus the presence of any intramolecular hydrogen bonds in nonamethylferrocenylcarbinols with bulky substituents, (e.g. Mes) is excluded.

The number of conformations stabilized by the intramolecular hydrogen bonds, as observed in the IR spectra, is consistent with the results of the conformational analysis. The number of absorption bands corresponding to H-bonded OH groups

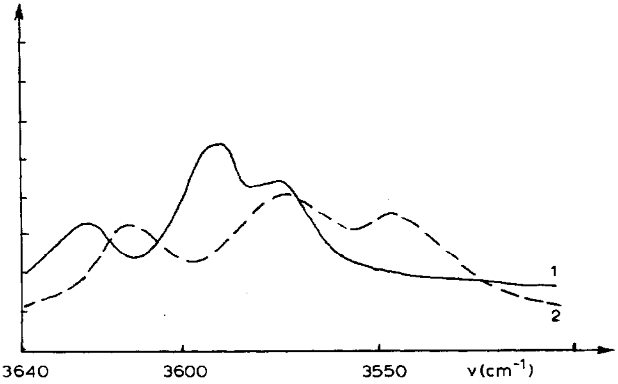

Fig. 3. IR spectra of FcCHROH solutions in cyclohexane ($c = 2 \times 10^{-2}$ mol/l, $d = 0.2$ cm); 1, R = Me (IIb); 2, R = Ph (IIc).

indicates that there are two types of intramolecular hydrogen bonds in the secondary ferrocenylcarbinols IIb–IId, and only one in the corresponding nonamethylferrocenylcarbinols (Table 1). In complexes IIa, IIe there is only one type of H-bonded OH group and in the corresponding methylated molecules there are no intramolecular hydrogen bonds at all.

The type of OH-group coordination in ferrocenylcarbinols was established by comparison of the spectra of compounds with different R substituents and by estimation of their relative abilities to form intra- and intermolecular hydrogen bonds (Tables 1, 2).

The IR spectra of ferrocenylcarbinols with aliphatic (CH_3 (IIb)) and aromatic (C_6H_5, C_6F_5 (IIc,d)) substituents at the carbinol C atom are similar, which means that the ν_1 bands can be assigned to the intramolecular OH ··· π(Cp) hydrogen bonds, and the ν_2 bands can then be assigned to the OH ··· Fe bonds (Fig. 3). For cases in which only one absorption band, due to the H-bonded OH groups, was observed, the nature of the intramolecular hydrogen bonds in ferrocenylcarbinols was inferred from the results of an analysis of the correlation between the $\Delta\nu$(OH) shifts for intra- and those for intermolecular H-bonds (DMSO was the acceptor in the latter). Figure 4 shows the symbatic change of these shifts for both ν_1 and ν_2 bands in the carbinols IIb–IId. It is clearly seen that $\Delta\nu$(OH) for carbinol IIa turns out to be near to the curve corresponding to ν_1. The $\Delta\nu$(OH) values for IIe and IIf lie on the curve corresponding to ν_2. This suggests that in the ferrocenylcarbinol IIa the intramolecular OH ··· π hydrogen bond has been formed whereas in compounds with bulky substituents (IIe,f) the OH ··· Fe bond is formed. It is noteworthy that in the IR spectrum of the carbinol with R = Mes (IIe) along with the ν(bonded OH) band, the ν(free OH) absorption band is observed, whereas in spectra of the carbinol with R = Bu^t (IIf) there is no ν(free OH) band. Thus in accord with the conformational analysis for complex IIe, conformations with the intramolecular OH ··· Fe hydrogen bond in addition to those without such hydrogen bonds may exist, whereas for IIf the only possible conformation is one with OH-group coordinated by Fe atom.

Analysis of the plot, shown in Fig. 4, leads to the conclusion that the stability of the intramolecular hydrogen bond increases on going from electron-donating to

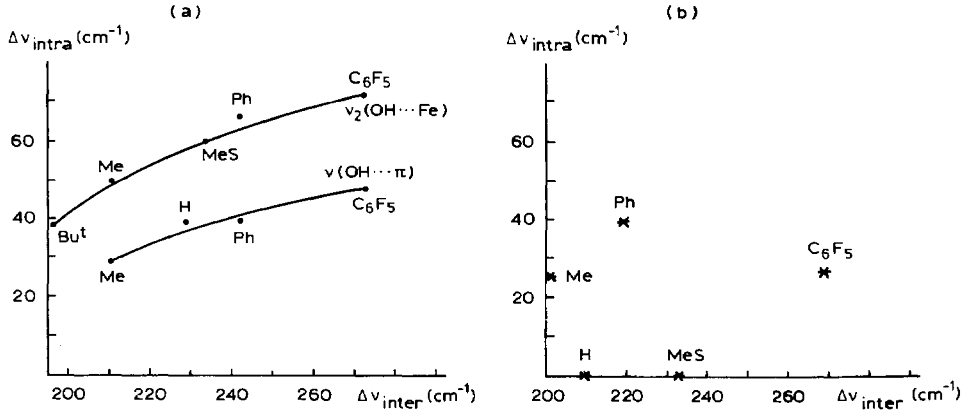

Fig. 4. Correlation between the $\Delta\nu$(OH shifts) upon formation of intramolecular hydrogen bonds and intermolecular hydrogen bonds (with DMSO) for FcCHROH (a) and ^{9}FcCHROH (b).

electron-accepting substituents. The ability to participate in the intramolecular H-bonds is symbatic with the proton-donating properties of the carbinols in the series: $\mathrm{Bu^t} < \mathrm{CH_3} < \mathrm{Mes} < \mathrm{C_6H_5} < \mathrm{C_6F_5}$ (H bonds of the OH ··· Fe type) and $\mathrm{CH_3} < \mathrm{H} < \mathrm{C_6H_5} < \mathrm{C_6F_5}$ (H bonds of the OH ··· π type).

In nonamethylferrocenylcarbinols the role of steric factors predominates, a fact which is reflected in the absence of a symbatic correlation between changes in the relative stabilities of the intra- and intermolecular H bonds (the $\Delta\nu$(OH) values) (Fig. 4), and a decrease in the number of conformations stabilized by the intramolecular hydrogen bonds. Since the results of the conformational analysis of ferrocenylcarbinols have been fully confirmed by the IR data, analogous calculations were used for the assignment of the ν(bonded OH) bands to H bonding with the Fe atom in spectra of the nonamethylferrocenylcarbinols. Weakening of the intramolecular hydrogen bond is indicated by the smaller values of $\Delta\nu$(OH) in the spectra of carbinols I compared with II (Table 1). The absence of intramolecular H bonds (no ν(bonded OH) bands observed), not only for Ie (R = Mes) but also for the considerably less-crowded complex Ia (R = H), is also interesting. In order to explain this fact one may assume that the weak OH ··· Fe hydrogen bond can be formed only if conformation, with OH group rotated towards the Fe atom, corresponds to the minimum (or to one of the minima) on the potential energy curve. This assumption is confirmed by the fact that the non-methylated analogue IIa has no preferable, sterically induced conformations and thus forms only OH ··· π H bonding. The fact that the OH ··· Fe bond stabilities are lower, whereas the formation constants (K_f) are higher for Ib–Id as compared with those of IIb–IId lends further support to the above assumption. The increase in K_f values, thus reflecting the predominance of those conformations which favour the OH ··· Fe bond, is consistent with a deepening of the energy minimum for Ib compared with that for IIb (Fig. 2). Thus steric factors bring about a preponderance of those conformations with intramolecular H bonds in complexes Ib–Id, and at the same time they cause a weakening in these bonds compared to those in non-methylated analogues.

Thus combination of an IR spectral study of the α-ferrocenylcarbinols with a conformational analysis allows some important conclusions to be drawn on the influence of the substituents on the structure of the isolated molecules, viz. on the orientation of the carbinol group relative to the metallocene nucleus. It also enables reliable assignments of the absorption bands in the IR spectra of ferrocenyl- and nonamethylferrocenylcarbinols to be made and reveals the influence of electronic and steric factors on the nature and stability of intramolecular hydrogen bonds.

Experimental

The compounds studied were prepared by published procedures [1].

IR spectra were recorded with an IR-75 spectrophotometer, in solutions of less than 2.5×10^{-2} M, $d = 0.2 = 2$ cm. The concentration of DMSO in the CCl_4 solution for estimation of proton-donating properties was 5×10^{-1} mol/l.

All calculations were carried out with a MOLBD3 program [15] on an EC 1061 computer. Cp-ligands were regarded as regular pentagons with fixed geometry, the Fe–Cp (centroid) distance was taken to be 1.650 Å. The parameters of potentials for C, H, O atoms were taken from [8]. Because parameters for non-bonded potentials involving the majority of metal atoms are not available from the literature at present we tried two procedures so as to take into account the changes in the substituent-metallocene energy: by (a) assuming the same non-bonded parameters for the Fe atom as for C (the same technique was used for the study of complexes with organic ligands [16]), and (b) ignoring non-bonded interactions of the metal atom. The corresponding curves were found to lie quite close to each other thus the major contribution to the increase in U_{conf} was the rotation of the substituent and its subsequent interaction with the ligand. In the U_{conf} vs. ϕ plots shown in Figs. 1 and 2 the non-bonded metal atom interactions were calculated by the first procedure using the parameters as those for the C atom.

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