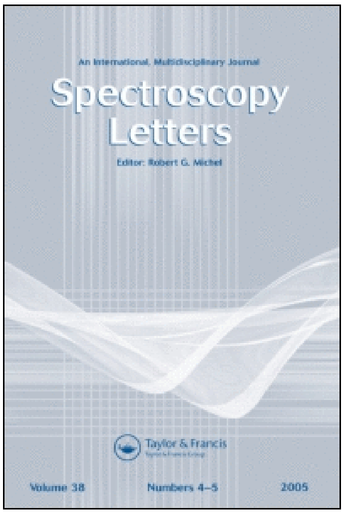

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STUDIES ON ORGANOMETALLIC COMPOUNDS BY FT–IR

Keywords: Ferrocene; inter–and intramolecular hydrogen bonding; benzene as solvent; IR spectra.

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ABSTRACTS

The different substituents of N–methylferrocene of aniline compounds were investigated by FT–IR spectrometer. On the basis of their IR data , the intra– and intermolecular hydrogen bonds between the hydrogen on nitrogen and ferrocenyl as well as benzene ring in molecules and benzene as solvent are discussed in solution of which CCl_4, benzene and cyclohexane as solvent. It has been found that the solvent and concentrations of the compounds greatly influence the forming of hydrogen bonding.

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INTRODUCTION

In molecules containing hydroxyl group, the s orbital of hydrogen in one molecule overlaps with p orbital of polar element(generally oxygen and nitrogen) in another molecule, then hydrogen bridge, which connects the two molecules tightly, is formed between the two molecules by hydrogen. We called it hydrogen bond. If there is a polar group Y except hydroxyl group in a molecules, and their steric distance is suitable, an intromolecular hydrogen bond can be formed.

Hydrogen bonding has been detected in many ways, including measurements of diple moments, solubility behavor,freezing-point lowering, and heats of mixing, but the most important way is by the effect of hydrogen bond on IR and other spectra. The IR frequencies of groups, such as O-H or C=O, are shifted when the group is hydrogen bonded. Hydrogen bonding always moves the peak toward lower frequencies. In many cases, in dilute solution, there is partial hydrogen bonding, that is, some OH groups are free and some are hydrogen bonded . In such case two peaks appear. Infrared spectroscopy can also distinguish between inter- and intramolecular bonding, since intermolecular peaks are intensified by an increase in concentration while intramolecular peaks are unaffected.

In the end of 1950s, when Trifan firstly discovered that the vibrational frequency of hydroxyl absorption lowers to 3574cm^{-1} in ferrocenyl compounds, scientists began to pay attention to the hydrogen bonding formed between hydroxy group and π-electron cloud. There is little difference between π-hydrogen bonds and general associated hydrogen bonds. The energies of π-hydrogen bonds are smaller than that of associated hydrogen bonds, the vibrational frequencies of π-hydrogen bonds are 15-50cm^{-1} lower than that of free hydroxy group. For instance , the υ_{OH} of cis-o-hydroxylphenol is 30cm^{-1} lower than that of its trans isomer.

It has been done a lot of work on the study of organometallic compounds by FT-IR. Semeriishin[1] studied hexacyanoferrates of aniline by IR; Marsegishvili [2]'s work of ferrocyanide and ferricyanide; Bencivenni [3], Phillips [4] and Feng Yan [5] use FTIR and Raman spectra to investigate ferrocene derivatives. There are also some reports [6—9] on intro – and inter – molecular hydrogen bonds in ferrocene.

EXPERIMENT

Spectra were obtained with a Nicolet 170SX FT – IR spectrometer. The thickness of liquid cell is 1mm. All reagents were A.R. grade, dried , redistilled.

Sample:	FcCH2NH – Ar – R (Fc: ferrocene)
I	$R=p-Cl$
II	$R=p-Br$
III	$R=p-CH_3$
IV	$R=H$
V	$R=m-NO_2$ (p: para; m: meta)

The samples were dissolved in tetrachloromethane(CCl_4), cyclohexane and benzene, respectively. Different concentrations of the samples in above solvents were obtained according to the amount of the samples dissolved.

RESULTS AND DISCUSSION

Intramolecular Hydrogen Bonding

From the data shown in Table 1 and 2, it can be seen that the compounds have strong adsorption in the range of 3413 – 3428cm^{-1} in CCl_4(10^{-1} mol * dm^{-3}) and cyclohexane solution. But in more dilute CCl_4 (10^{-2} – 10^{-3}mol * dm^{-3}) and cyclohexane solution, there are other weak adsorption ranging 3329cm^{-1} to 3340cm^{-1} except of 3413 – 3428 cm^{-1}. We consider the 3413 – 3428cm^{-1} as free stretching adsorption of N – H bond and 3329 – 3340cm^{-1} as the adsorption of intramolecular hydrogen bonds between the hydrogen of N – H and benzene ring (see Table 3).

TABLE 1

The IR Data of N – H Adsorption (CCl_4 as Solvent)

I	C	1.075×10^{-1}	1.153×10^{-2}	1.443×10^{-3}
	W	$3418.5cm^{-1}$	$3418.3cm^{-1}$ $3400.0cm^{-1}$	$3420.5cm^{-1}$ $3397.2cm^{-1}$
II	C	1.295×10^{-1}	1.064×10^{-2}	7.703×10^{-3}
	W	$3414.1cm^{-1}$	$3413.4cm^{-1}$ $3398.1cm^{-1}$	$3416.2cm^{-1}$ $3398.2cm^{-1}$
III	C	1.440×10^{-1}	1.424×10^{-2}	7.402×10^{-3}
	W	$3421.1cm^{-1}$	$3421.1cm^{-1}$	$3421.7cm^{-1}$
IV	C		1.003×10^{-2}	3.661×10^{-3}
	W	*	$3421.2cm^{-2}$ $3398.2cm^{-1}$	$3427.1cm^{-1}$ $3414.0cm^{-1}$
V	C		1.252×10^{-2}	6.801×10^{-3}
	W	*	$3428.3cm^{-1}$	$3425.3cm^{-1}$ $3413.5cm^{-1}$

* can't be dissolved; C: concentration(mol × dm^{-3});
W: wavenumber

TABLE 2

The IR Data of N – H (Benzene and Cyclohexane as Solvent)

		I	II	III	IV	V
H	C(× 10^{-3})	1.942	4.334	5.687	5.181	6.272
	W(cm^{-1})	3420.5	3419.8	3420.8	3420.4	3418.8
		3405.7	3408.5	3409.8	3408.0	3405.2
		3399.9	3392.4	3393.7		3426.8
B	C(× 10^{-3})	1.859	6.986	6.884	6.146	6.762
	W(cm^{-1})	3413.2	3408.2	3408.4	3410.6	3410.2
		3392.2		3392.2	3398.8	
		3419.8		3419.8	3424.4	

H: cyclohexane as solvent; B: benzene as solvent
C: concentration(mol × dm^{-3}); W: wavenumber

TABLE 3

Interpretation of the Adsorption Frequencies

Wavenumber	Interpretation
3413 – 3428cm^{-1}	Free N – H adsorption
3413 – 3414cm^{-1}	Hydrogen bonding between hydrogen of N – H and cyclopentadienyl
3405 – 3409cm^{-1}	Hydrogen bonding between hydrogen of N – H and ferro in ferrocene
3392 – 3400cm^{-1}	Hydrogen bonding between hydrogen of N – H and benzene ring

In the solution of which cyclohexane as solvent, all compounds studied have small peaks between 3405 – 3409cm^{-1}. These peaks belong to the adsorption of intramolecular hydrogen bonds between the hydrogen of N – H and ferro in ferrocene. The compounds of IV and V have weak adsorptions in 3413 – 3414 cm^{-1} in CCl_4 solution. These peaks belong to the intramolecular hydrogen bonds between hydrogen of N – H and cyclopentadienyl (see Table 3).

Being a strong electron acceptor, CCl_4 can form electric charge transfer(CT) complexes with ferrocene compounds which are electron donors. In higher concentration (10^{-1}mol * dm^{-3}), the ferrocene compounds mainly exist as CT complexes with CCl_4. Because of the steric hindrance, N – H has little probability to form intramolecular bonding and mainly exists in free state. Therefore, there is only one N – H stretching adsorption peak.

In more dilute solution, the probabilities to form CT complexes decrease because of decreasing of the solvend particles, then, N – H has the probability to form weak intramolecular bonding with benzene ring in the molecule. the properties of benzene substituents would influence the formings of intramolecular bonding. the ferrocene compounds have weak adsorptions in the range of 3398 – 3400cm^{-1} when they have donor substituents(such as CH_3, H) in dilute CCl_4 solution (about 10^{-2}mol * dm^{-3}). In this case, the adsorption is more intense when the benzene substituents is CH_3 comparing with H. The compounds nearly haven't the weak adsorption when the benzene substituents are Cl and NO_2. In conclusion, when benzene ring has the electron donor substituents, its density of electron cloud is increased and the ability to combine with hydrogen is strengthened, but acceptor substituents decrease the density of benzene ring electron cloud and the benzene ring has lower or no ability to combine with hydrogen to form intramolecular bonding.

When Br is being the substituent of benzene, it has stronger resonance than that of Cl except of its electron acceptor property. Therefore, the adsorption of the intramolecular bonding between the benzene ring and hydrogen of N – H in spectra can be detected.

For the compounds IV and V, there are bigger steric hindrance comparing to compounds I – III due to their large volume of the substituents, then, they have adsorptions in the range of 3413 – 3414cm^{-1} in 10^{-3}mol * dm^{-3} CCl_4 solution. Otherwise, the acceptor properties of their substituents decrease the probabilities of forming intramolecular bonding between benzene ring and hydrogen of N – H and increase the probabilities of that between hydrogen of N – H and cyclopentadienyl.

Cyclohexane cann't form CT – complexes with methylferrocene of aniline, so that there appear fine structures in spectra. There isn't any intermolecular bonding because of the much dilute solution of compounds in cyclohexane, but the ferro and benzene ring can form intramolecular bonding.

It is easy that ferro in ferrocene loses an electron and becomes ferrocene cation. From the ionization potential of benzene and ferrocene(ferrocene, 7.05ev; benzene ring, 9.2ev), it can be seen that ferro in ferrocene is easier than benzene ring to form hydrogen bonding. The adsorption frequencies of ferro's hydrogen bonding are higher than that of benzene ring's in spectra.

Intermolecular Hydrogen Bonding In the solution of which benzene as solvent, The strong peaks appeared in the solution of which CCl4 and cyclohexane as solvents become as weak peaks or disappear. The strongest peaks appear in the range of 3408 – 3413cm^{-1}. The peaks become broader and the fine structures disappear.

Being a solvent, like the benzene ring in the molecules, benzene can form hydrogen bonding with the hydrogen of N – H in ferrocene compounds. Then, the ferrocene compounds can form intramolecular hydrogen bonding as well as intermolecular hydrogen bonding with solvent. the adsorption in the range of 3408 – 3413cm^{-1} belongs to interreaction of intra – and intermolecular hydrogen bonding. The broaden peaks demonstrate the influence of intermolecular hydrogen bonding.

In a word, the weak peaks in the range of 3392 – 3390cm^{-1} has been considered as intramolecular hydrogen bonding of benzene ring and hydrogen of N – H, and the adsorption of 3419 – 3424cm^{-1} as the free stretch vibrations of N – H. Therefore, in the solution of which benzene as solvent, the main interreaction is the solvend and the solvent, not the above two kinds of adsorptions.

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