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Abstract

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DETERMINATION OF THE STRUCTURE OF CERTAIN ISOMERIC DISUBSTITUTED FERROCENES FROM IR ABSORPTION SPECTRA

We have obtained disubstituted ferrocene derivatives—amides of alkyl- and phenylferrocenecarboxylic acids and nitriles of alkylferrocenecarboxylic acids. To establish the structure of the isomers obtained, measurements of oxidation-reduction potentials, UV spectra, and comparative adsorption capacity on Al_2O_3 were used.*

In the present work we studied the IR spectra of the disubstituted ferrocenes obtained and used them to establish the structure of the isomers.

On the basis of a study of the IR spectra of a large number of different monosubstituted ferrocenes in crystals and solutions (1) and a calculation of the vibrations of the cyclopentadienyl rings of ferrocene (2), it was shown that the totally symmetric vibration of the unsubstituted cyclopentadienyl ring is characteristic in frequency and shape, and that the absence of absorption in the region 1100-1110 cm^{-1} is a reliable criterion for identifying heteroannular disubstituted compounds. Some heteroannular disubstituted ferrocenes (3,4), as well as the heteroannular ferrocenylamides obtained by us, absorb in this region; however, this absorption is not associated with a vibration of the unsubstituted ring. We have shown (1) that measurement of the integral intensity makes it possible to distinguish the band of the totally symmetric vibrations of unsubstituted cyclopentadienyl rings from other bands close in frequency in the IR spectrum. Like the authors of a number of earlier studies (4–6), we also observed in the spectra of heteroannular disubstituted ferrocenes the absence of an absorption band in the region 1000-1010 cm^{-1}, characteristic of unsubstituted cyclopentadienyl rings.

Studies of homoannular acetylalkyl-, acetylaryl-, and diarylferrocenes (4,6,7) showed the possibility of identifying 1,2- and 1,3-isomers from their IR spectra. The authors of these works observed, in the spectra of solutions of 1,2-isomers in chloroform, an absorption band in the region 910-920 cm^{-1}; in the spectra of 1,3-acetylalkylferrocenes, a doublet in the region 900-925 cm^{-1}; and in the spectra of 1,3-acetylaryl- and 1,3-diarylferrocenes, a doublet at 897-905 cm^{-1}.

Fig. 1. IR spectra of amides of isomeric methylferrocenecarboxylic acids in crystals.

Figure 1: Fig. 1. IR spectra of amides of isomeric methylferrocenecarboxylic acids in crystals.

Although the position of the absorption bands assigned by the authors to the 1,2- and 1,3-isomers may depend on the type of substituents, in our view the essential point is that, in the same frequency region that is characteristic for 1,3-isomers, absorption bands are observed in the spectra of the corresponding mono- and heteroannular disubstituted compounds. This regularity was used by us in considering the spectra of the isomeric disubstituted ferrocenes studied. As can be seen from the measurement results given in Table 1, in the spectra of mono- and heteroannular disubstituted compounds one or two bands of medium intensity are observed in the region 910–920 cm^{-1}. In the spectra of the pairs of homoannular isomers that we studied, a difference is observed in this region. In the spectra of some isomers there is an absorption band in the region 910–920 cm^{-1}; moreover, for these isomers charactern, the presence of one more band or a doublet at 930–950 cm^{-1} is characteristic. In the spectra of the other isomers, absorption in the region 900–950 cm^{-1} is completely absent, and weak bands are observed at 880–890 and 950–970 cm^{-1}. On the basis of these data we assigned isomers of the first type to the 1,3-substituted compounds, and isomers of the second type to the 1,2-substituted compounds. Identification of 1,2- and 1,3-phenylferrocenylamides by this region of the spectrum is difficult.

Fig. 1. IR spectra of amides of isomeric methylferrocenecarboxylic acids in crystals.
a $-1,1'$-$CH_3C_5H_4FeC_5H_4CONH_2$,
b $-1,3$-$CH_3(CONH_2)C_5H_3FeC_5H_5$,
c $-1,2$-$CH_3(CONH_2)C_5H_3FeC_5H_5$

Further confirmations of the correctness of the assignment made were obtained by considering the frequencies and intensities of the bands characteristic of the $C=O$ and NH_2 groups (see Figs. 1, 2). In the spectra of ferrocenylamide and heteroannular alkyl- and phenylferrocenylamides, two intense amide bands are observed at 1647–1663 and 1603–1610 cm^{-1}, of which the first

Table 1

* The works of A. N. Nesmeyanov, E. G. Perevalova, and others are in *Izv. AN SSSR, ser. khim.*, in press.

Compound	M.p., °C	Characteristic frequencies in IR spectra (crystals)						
$C_5H_5FeC_5H_5$	—	—	—	—	—	—	1001	1107
$CH_3C_5H_4FeC_5H_5$	35–36	880	—	923	—	—	1002	1106
$C_2H_5C_5H_4FeC_5H_5$	oil	880	—	906	—	—	1000	1106
$C_6H_5C_5H_4FeC_5H_5$	114–115	885	—	909	—	—	1000	1105
$CONH_2C_5H_4FeC_5H_5$	168–170	—	—	912	—	—	1007	1110
$CNC_5H_4FeC_5H_5$	107–108	—	899	912	—	—	1005	1108
$1,1'-CH_3C_5H_4FeC_5H_4CONH_2$	145–146	880	—	914–921	—	—	—	—
$1,1'-C_2H_5C_5H_4FeC_5H_4CONH_2$	141–142	880	—	908	—	—	—	—
$1,1'-C_6H_5C_5H_4FeC_5H_4CONH_2$	127–128	890	—	912	—	—	—	—
$1,1'-CH_3C_5H_4FeC_5H_4CN$	72–73	880	899	911–924	—	—	—	—
$1,1'-C_2H_5C_5H_4FeC_5H_4CN$	29–30	—	—	908–915	—	—	—	—
$1,2-CH_3(CONH_2)C_5H_3FeC_5H_5$	119–120	878–890	—	—	—	970	1005	1107
$1,2-C_2H_5(CONH_2)C_5H_3FeC_5H_5$	95–96	884–890	—	—	—	950–962	1003	1108
$1,2-CH_3(CN)C_5H_3FeC_5H_5$	51–52	886–893	—	—	—	964	1004	1107
$1,2-C_2H_5(CN)C_5H_3FeC_5H_5$	oil	885	—	—	—	952–963	1005	1107
$1,3-CH_3(CONH_2)C_5H_3FeC_5H_5$	146–147	—	—	918	946	—	1006	1107
$1,3-C_2H_5(CONH_2)C_5H_3FeC_5H_5$	161–162	—	—	914	931	—	1003	1107
$1,3-CH_3(CN)C_5H_3FeC_5H_5$	45–46	—	897	911	926, 944	—	1003	1106
$1,3-C_2H_5(CN)C_5H_3FeC_5H_5$	oil	—	—	916	932	—	1003	1107
$C_6H_5(CONH_2)C_5H_3FeC_5H_5$	219–220	890	—	922	933	955	1003	1106

Fig. 2. IR spectra of isomeric amides of ethylferrocenecarboxylic acids in CCl_4 solution: a—1,1′-$C_2H_5C_5H_4FeC_5H_4CONH_2$; b—1,3-$C_2H_5(CONH_2)C_5H_3FeC_5H_5$; c—1,2-$C_2H_5(CONH_2)C_5H_3FeC_5H_5$

Figure 2: Fig. 2. IR spectra of isomeric amides of ethylferrocenecarboxylic acids in CCl_4 solution: a—1,1′-$C_2H_5C_5H_4FeC_5H_4CONH_2$; b—1,3-$C_2H_5(CONH_2)C_5H_3FeC_5H_5$; c—1,2-$C_2H_5(CONH_2)C_5H_3FeC_5H_5$

Compound	M.p., °C	Characteristic frequencies in IR spectra (crystals)					
$C_6H_5(CONH_2)C_5H_3FeC_5H_5$	181–182	897	928	–	–	1003	1106

belongs to $\nu C = O$, and the second to δ-NH_2 vibrations. In the region of NH stretching vibrations, bands are observed that are characteristic both of free (3400–3470 cm^{-1}) and of bonded (3170–3300) NH groups. This is explained by the formation of intermolecular hydrogen bonds in the crystals. In solutions of these compounds the hydrogen bonds are destroyed, and the spectra contain only two bands, 3423 and 3540 cm^{-1}, assigned respectively

but to symmetric and antisymmetric vibrations of free NH groups. Introduction of a second substituent into the cyclopentadienyl ring can influence the ability of the amide group to form intermolecular hydrogen bonds, and this influence should depend on the relative positions of both substituents. It is obvious that in the case of the 1,2-configuration this influence will be considerably greater than in the 1,3-isomers. Indeed, in the spectra of alkylferrocenylamides which, on the basis of the character

Fig. 2. IR spectra of isomeric amides of ethylferrocenecarboxylic acids in CCl_4 solution:
a —1,1′-$C_2H_5C_5H_4FeC_5H_4CONH_2$,
b —1,3-$C_2H_5(CONH_2)C_5H_3FeC_5H_5$,
c —1,2-$C_2H_5(CONH_2)C_5H_3FeC_5H_5$

of absorption in the region 900-1000 cm^{-1} we consider to be 1,2-isomers, a substantial difference is observed in the regions 1600–1700 and 3100–3500 cm^{-1}. In the spectra of these compounds there occurs a splitting of the band of deformation vibrations of the NH_2 group (the assignment was confirmed by comparison with the spectra of deuterated compounds). At the same time, in the region of NH stretching vibrations, in most cases the degree of splitting of the bands decreases. These changes are connected with a different character of the hydrogen bonds in the 1,2-derivatives. The same spectral picture is also observed for homoannular phenylferrocenylamide, m.p. 181–182°. The solution spectra of 1,2-substituted compounds in this region prove to be very similar and contain absorption bands of both free and bonded NH groups.

Table 2

Compound	m.p., °C	ν max, cm^{-1}	$A \cdot 10^{-4}$, $l \cdot mol^{-1} \cdot cm^{-2}$
$CONH_2C_5H_4FeC_5H_5$	168–170	1685	4.70
1,1′-$C_2H_5C_5H_4FeC_5H_4CONH_2$	141–142	1686	5.10
1,3-$C_2H_5(CONH_2)C_5H_3FeC_5H_5$	161–162	1683	5.10
1,2-$CH_3(CONH_2)C_5H_3FeC_5H_5$	119–120	1682	4.72
1,2-$C_2H_5(CONH_2)C_5H_3FeC_5H_5$	95–96	1680	4.85

In the case of isomers to which the 1,3-configuration was assigned, splitting of the δ-NH_2 band is not observed for methylferrocenylamide and for the second isomer of homoannular phenylferrocenylamide with m.p. 219–220°. In 1,3-ethylferrocenylamide, splitting of this band is observed (although much less profound), which can be explained by the ability of the ethyl radical, owing to its larger size, to influence the amide group even in the 1,3-arrangement. The solution spectra of the 1,3-isomers in CCl_4 are very similar to the solution spectra of the corresponding 1,1′-derivatives and are characterized by the absence of bands of bonded NH groups.

The isomers studied also differ in the integral intensities of the amide carbonyl band. From the results given in Table 2 it is seen that the ethyl group, as an electron donor, in the 1,1′- and 1,3-isomers increases the integral intensity of the carbonyl band in comparison with the value found for the amide of ferrocenecarboxylic acid. This effect is not observed in the case of 1,2-methyl- and ethylferrocenylamides, which is evidently connected with loss of conjugation of the amide group with the cyclopentadienyl ring as a result of steric hindrance in these compounds.

Thus, examination of the characteristic absorption bands of the isomeric disubstituted ferrocenes studied in different spectral regions leads to concordant results, which makes it possible to use IR spectra to establish the structure of these isomers.

The data obtained by us agree with the results of studies of oxidation–reduction potentials, UV spectra, and comparative adsorption ability on Al_2O_3 in a series of amides and nitriles of alkylferrocenecarboxylic acids. Further investigations are being carried out for the final establishment of the structure of homoannular amides of isomeric phenylferrocenecarboxylic acids.

The IR spectra of the substances studied were measured on a double-beam UR-10 IR spectrometer in the region from 400 to 4000 cm^{-1}, with KBr, NaCl, and LiF prisms, in crystals with Vaseline oil and in solutions in CCl_4, CS_2, and dioxane. The integrated intensities of the carbonyl bands were measured in CCl_4 solution by the procedure used by us in the preceding investigation ([1]).

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Note: Figure translations are in progress. See original paper for figures.