INFRARED SPECTRA OF SOME ALKYLFURANS

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 3, pp. 291–293, 1970

UDC 547.722.2:543.422.4

The possibility of using the region of the C=C and C—H vibrations of the furan ring for the analysis of the structure of substituted furans and the possibility of determining the structure of the side chain in alkylfurans and alkylbenzofurans have been shown.

The development of investigations on the catalytic alkylation of furan compounds is complicated by the absence of reliable methods for analyzing the reaction products. Our work [1] has shown that the separation of the reaction products, the determination of their purity, and their identification with reference substances can be carried out successfully by GLC. However, this method does not make it possible to determine the structure of a substance, the number of substituents, nor their structure or position in the furan ring. These questions can apparently be answered by means of spectroscopy, in particular IR spectroscopy. For this purpose it was necessary to find some characteristic features in the IR spectra of alkyl derivatives of furan and benzofuran: the influence of the position and number of the substituents on the main vibrations of the furan ring, and also the influence of the ring on the frequency of the substituent.

As the subjects of our investigation we select 2- and 3-monoalkylfurans, 2,5-di-tert-butylfuran, and 2-tert-butylbenzofuran, which may be regarded as a trisubstituted furan.

Our main attention was devoted to those regions of the spectrum which, in our opinion, could be useful for answering the questions posed. This is the region of the C=C stretching vibrations of the furan ring, which consists of two planar vibrations, i.e., the in-phase $\nu_{C=C}s$ and the antiphase $\nu_{C=C}as$ vibrations, and the region of the C—H stretching vibrations of the ring and the radical [2, 3].

Table 1 gives the frequencies of the C=C and C—H vibrations of the furan ring and the ratios of their intensities. On passing from furan to the 2-alkylfurans the position of the $\nu_{C=C}as$ band is practically unchanged, while the $\nu_{C=C}s$ band is shifted slightly in the short-wave direction. The ratio of the intensities of these bands in 2-alkylfurans is almost one and one-half times as great as in furan. In 3-alkylfurans there is a tendency toward a shift in the long-wave direction for the $\nu_{C=C}as$ band and for the $\nu_{C=C}s$ band there is a slight shift in the short-wave direction. The ratio of the intensities of these bands is the same as in furan. In 2,5-di-tert-butylfuran the $\nu_{C=C}s$ band undergoes a very marked displacement in the high-frequency direction ($\Delta\nu$ 75 cm^{-1}), while the position of the $\nu_{C=C}as$ band does not change from that in furan. The ratio of the intensities $I_{\nu_{C=C}as}/I_{\nu_{C=C}s}$ decreases by a factor of about 1.5 compared with furan. Benzofuran and 2-tert-butylbenzofuran have a single band in this region.

Table 1. Position and Ratio of the Intensities of the Bands of the Anti- and In-Phase Vibrations of the C=C Bonds and the C—H Vibrations of the Furan Ring in Alkylfurans

Compound	$\nu_{C=C}^{as}$, cm^{-1}	$\nu_{C=C}^{s}$, cm^{-1}	I_{as}/I_s	ν_{C-H}, cm^{-1}	ν_{C-H}, cm^{-1}	I_1/I_2
Furan	1595	1490	0.62	3120	3150	0.86
2-tert-Butylfuran	1595	1515	0.88	3120	3150	0.33
3-tert-Butylfuran	1570	1510	0.63	3110	3140	1.5
2-tert-Amylfuran	1595	1515	0.82	3120	3150	0.25
3-tert-Amylfuran	1570	1510	0.52	3110	3140	1.2
2-Isobutylfuran	1600	1515	0.85	3120	3150	0.37
2-Methylfuran	1610	1520	0.4	3120	3150	0.44
2-n-Butylfuran	1600	1510	0.90	3120	3150	0.36
2-sec-Butylfuran	1595	1510	0.82	3120	3150	0.38
2,5-di-tert-Butylfuran	1610	1565	0.37	3110	—	—
Benzofuran	1616	—	—	3120	3150	0.7
2-tert-Butylfuran	1590	—	—	3120	—	—

In examining the IR spectra of the 2- and 3-monoalkyl- and 2,5-dialkylfurans, and also those of benzofuran and 2-tert-butylbenzofuran, a change in the intensity of the C—H vibration of the furan ring in the 3100–3200-cm^{-1} region as a function of the position of the substituent was observed.

It is known [4,5] that in this region furan and benzofuran have two bands (3120 and 3150 cm^{-1}) of similar intensities. They apparently relate to the stretching vibrations of the β- and α-C—H bonds, respectively, of the furan ring.

In 2-alkylfurans two bands are observed with the same frequencies, but the intensity $I_{\nu_{3150}}$ is 2–2.5 times greater than that of $I_{\nu_{3120}}$. 3-Alkylfurans have bands at 3110 and 3140 cm^{-1}, characterizing the C—H vibrations of the furan ring. Their relative intensity is opposite to that of 2-alkylfurans.

The change in the intensities of the C—H-stretching vibrations of the furan ring as a function of the position of the substituent is due to the fact that the vibrations of the C—H bonds in the furan ring are nonequivalent dynamically and differ in their mechanics, and each is determined by its own band. This is seen in 2,5-di-tert-butylfuran, in which the α-C—H band is absent, while in the 3100–3200 cm^{-1} region there is only one band, at 3120 cm^{-1}, which is due to the β-C—H bonds. 2-tert-Butylbenzofuran also has only one band in this region.

Thus, the position of the substituents and their number has a fundamental influence on the behavior of the bands of the C=C and C—H stretching vibrations of the furan ring and their intensities. This fact may be of great assistance in the analysis of the structures of furan compounds.

We have examined the influence of the heteroaromatic ring on the side chain in alkylfurans with substituents having an iso structure. It has been shown previously for alkylfurans with substituents of normal structure [6] that the introduction of a heteroatom into the molecule substantially lowers the intensity of the bands of the stretching vibrations of the CH_2 and CH_3 groups of the side chain as compared with the alkanes. In this work we measured the intensities of the doubly degenerate stretching vibrations of the CH_3 group in alkylfurans and the alkylbenzofurans by Jones's method [7]. In addition, we calculated the intensities of this band for our compounds by Lopatin and Yakovlev's method, taking account the distance of each methyl group from the heteroatom (Table 2). The values of the intensities of the doubly degenerate stretching vibrations of the CH_3 groups found experimentally and by calculation are similar.

Table 2. Positions and Intensities of the Bands of the Doubly Degenerate Stretching Vibrations of the CH_3 Groups in Alkylfurans

Compound	ν_{CH_3}, cm^{-1}	$\varepsilon_{\mathrm{exp.}}$	$\varepsilon_{\mathrm{calc.}}$
2-tert-Butylfuran	2962	249	240
3-tert-Butylfuran	2958	300	330
2,5-Di-tert-butylfuran	2965	535	480
2-tert-Amylfuran	2963	290	270
3-tert-Amylfuran	2961	325	350
2-Isobutylfuran	2965	190	210
2-sec-Butylfuran	2970	176	190
2-tert-Butylbenzofuran	2970	220	240

It has been shown that a heteroatom considerably reduces the intensity of the absorption band of the double degenerate stretching vibrations of the CH_3 groups of a branched side chain. With an increase in the distance of the methyl group from the heteroatom, the intensity of the corresponding band rises, approximating to the intensity in the spectra of the alkanes. This is particularly true for 3-alkylfurans.

This method may be useful in determining the structures of side chains in alkylfurans.

EXPERIMENTAL

The spectra of the compounds studied were obtained on a UR-10 spectrometer in the 700–1800-cm^{-1} and 2700–3200-cm^{-1} regions. The measurement of the intensities of the C—H stretching vibrations was carried out in CCl_4 solutions in cells of constant thickness as described previously [8].

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9 February 1968

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