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IR SPECTRA OF SOME 2-, AND 3-SUBSTITUTED FURAN DERIVATIVES

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Research on 2- and 3- monosubstituted furan derivatives has not been able to establish accurately the site of substitution in the furan ring on the sole evidence of ring deformation vibrations maxima in the region of 1000-700 cm^{-1}, so that interpretation of the IR spectra have to be supplemented by chemical evidence of the structure of the compounds in question. In an effort to find more IR-spectroscopic criteria of the presence of the furan ring and of its substitution pattern, we investigated the ranges of 1800-1400 cm^{-1} and 1000-700 cm^{-1} in the spectra of several 2- and 3-substituted furyl alkenes and furyl carbinols in the hope of detecting maxima representing overtones and combination bands, and establishing a relation between their localization and intensity and the structure of the molecule, as has been done in the case of benzene and pyridine

Absence of studies on this subject in the literature relating to furan is probably due to particular interest in furan derivatives incorporating the carbonyl and the nitro groups, which hinder observation of the maxima referred to.

The compounds used in the investigations were: furan (I), 2-isopropenyl furan (II), 3-isopropenyl furan (III), 1-(1-butyl)-1-(2-furyl)ethylene (IV), 2-(2-furyl)hexene-2, [mixture cis:trans 2:3 (V) and 1:5 mixture of the same (VI)], 2-acetylfuran oxime (VII), furfural oxime (VIII), 1-cyano-2-(2-furyl)-ethylene (cis:trans 1:1) (IX), 2-furylcarbinol (X), 3-furylcarbinol (XI), dimethyl-(2-furyl)carbinol (XII), dimethyl-(3-furyl)carbinol (XIII), methyl-(1-butyl)-(2-furyl)-carbinol (XIV), and 2-methyl-1-butene (XV).

We have prepared all compounds and their purity (excepting IV, VII, VIII, and XI) was additionally confirmed by gas chromatography.

Observation of the region of 1800-1400 cm^{-1} in the IR spectra of the compounds in point with the C=C or C=N group in the side chain indicates two maxima, within the range of 1738-1705 cm^{-1} and 1698-1670 cm^{-1}, which cannot be explained with the aid of the IR spectroscopic data on furan derivatives reported in the literature.

Comparison with the spectra of furan (I) and 2-methyl-1-butene (XV) suggests the maxima as undoubtedly connected with a furan ring in the molecule. Their presence beside the visible maxima characteristic of furan seems to indicate that they may represent overtones of deformation vibrations of the CH bond in the furan ring, or some combination bands of these vibrations.

Characteristic bands at 1738-1654 cm^{-1}, 1551-1525 cm^{-1} and 1000-700 cm^{-1} of furan ring

Compounds Nr	Overtones β of the ring or combination bands β and γ CH of the ring			γ CH or β of the ring		
	a	b	c	d	e	f
I	1719 w	1698 w	-	974 s	854 m	715 s
II	1715 w	1672 m	-	923 m	858 s	783 m
III	1715 m	1672 w	-	950 m	858 s	769 m
IV	-	1698 w	-	947 w	862 m	757 m
V	1705 w	1674 m	-	930 w	864 s	772 m
VI	1705 w	1676 w	-	930 w	864 s	772 m
VII	1738 w	1691 w	-	938 s	872 s	806 w
VIII	1738 w	1691 w	-	951 s	869 m	796 s
IX	1698 w	1670 w	-	936 m	862 w	789 w
X	1718 w	1659 m	1551 m	944 m	888 m 886 m	788 s
XI	1718 w	1654 m	-	955 m	850 m	760 s
XII	-	1673 m	1525 w	932 m	884 w 844 w	758 m
XIII	-	1675 m	1525 w	944 w	884 m 845 m	750 s
XIV	1705 w	1659 w	1528 w	914 m dublet	864 w 837 w	780 m
XV	-	-	-	-	859 m	-

Bak, Brodersen, and Hansen's$^{5)}$ investigations on the IR spectra of furan and deuterofuran indicate the presence of two maxima, at 1700 cm^{-1} and 1729 cm^{-1}. These authors suggest that they represent either the first overtone of the vibration of the γCH bond in the ring (2 x 874) or a combination band of the deformation vibration of the CH bond in the ring and an undefined vibration of the ring (720 + 995). The maxima we are concerned with may be explained similarly it seems. Eminent agreement between the actual position of the maxima and that calculated (according to the suggestion by Bak et al) from the wave numbers of vibrations in the region of 1000-700 cm^{-1} confirms our surmise.

The maxima in the frequency ranges of 1675-1654 cm^{-1} and 1551-1525 cm^{-1} in the spectra of the furyl carbinols investigated (excepting XI) may also be regarded as representing certain combination bands or overtones. Characteristic is the intensity of the higher frequency (1675-1654 cm^{-1}) maxima, which equals that of the neighbouring maxima of ν vibrations of the furan ring (1607-1585 cm^{-1}).

The higher-frequency (1715 cm^{-1}) maxima for isomers (II) and (III) have respectively weak and medium intensities, conversely to the lower-frequency (1672 cm^{-1}) maxima.

For (VI) the intensity of all maxima in the region of 1800-1400 cm^{-1} is lower than for (V).

The maxima in point, in exactly corresponding positions, differ distinctly and significantly in intensity between the isomers (II) and (III), and between the mixtures of geometrical isomers (V) and (VI), which invites search for the same relationship in other compounds.

The spectra of none of the compounds investigated show in the region of 1000-700 cm^{-1} features that might be regarded as characteristic of a specified site of substitution in the ring, and the maximum for the γCH bond in the furan ring occurs for isomers (II) and (III) at the same frequency ($858\ cm^{-1}$).

The maxima found in the region of 1800-1400 cm^{-1} supplement the set of maxima characteristic of the furan ring. Further investigations will show whether they are a valuable criterion for the defining of the structure of some furan derivatives.

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