

INFRARED ABSORPTION SPECTRA OF FUNCTIONAL DERIVATIVES OF 5-NITROFURFURYL-2-POLYALKENES AND INTRAMOLECULAR INTERACTION

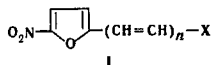
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The frequency characteristics of the vibration spectra of a number of polyalkene derivatives of 5-nitrofurans are examined. In particular, the IR spectra vibrations frequencies of the furan ring, nitro group, double bonds, and carbonyl group are examined with respect to the near and more remote intramolecular environment. The effects of intramolecular interaction, transmitted both through a chain of a 2-substituted system of the polyene type, and through a system of furan ring double bonds, are determined. The problem of the aromaticity of the furan ring is considered.

Continuing previously commenced research on study of methods of synthesizing [1-7] and physico-chemical properties (UV absorption spectra and Raman spectra) [8, 9] of functional derivatives of 5-nitrofuryl-2-polyalkenes (I), the present paper deals with the frequency characteristics of these compounds in the infrared absorption spectra over the range of frequencies 700-1800 cm^{-1} .



$n = 0, 1, 2, 3, 4$; $X = \text{CHO}; \text{CH}(\text{OCOCH}_3)_2; \text{COCH}_3; \text{COOH}; \text{COOCH}_3; \text{COOC}_2\text{H}_5; \text{CH}=\text{NNHCOCH}_2\text{CN}; \text{CH}=\text{NNHCSNH}_2$, etc.

The results show that when the conjugated chain is lengthened the general character of the IR spectra of the series of polyenes studied is preserved inside each group, only comparatively small shifts being observed. The spectra of the compounds studied are quite complex. Still it is possible to effect comparatively sharp separation, in these spectra, of bands connected with vibrations of the main functional structural elements of the molecules under investigation. This can assist in clarifying interaction processes between those structural elements, e.g., the furan ring, the C=C bonds, the nitro group, and the substituent X.

Furan ring vibrations. The results of our study (see Table 1) are in good agreement with previous data for the vibration spectra of furan derivatives [10-15].

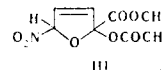
With our compounds we found the effect discovered, in the above references, of a substituent on the =C-O-C= vibration and C-H deformation vibration frequencies. In this connection it is of interest to note that introduction of an electron-accepting group such as the nitro group, which is much more active, than, for example, the methyl group, does not give rise to substantial changes in the frequency of these vibrations. This is illustrated by the data of Table 2.

As comparison of the spectra of 2-nitrofurans and 5-nitro-2-methylfurans shows (see Table 2), further substitution of the furan ring, introduction of a second substitution of the furan ring, introduction

of a second substituent at position 5, does not give rise to substantial changes in =C-O-C= bond vibration frequencies. It can be seen that in the case mentioned, the frequency of =C-O-C= symmetric vibrations changes somewhat more markedly than the frequency of the antisymmetric vibrations. With all the compounds which we investigated (see Table 1), these frequencies lie inside the limits 1010-1038 and 1234-1264 cm^{-1} .

On substitution furan ring vibration frequencies change comparatively little, as was previously found by other authors [15]. Our measurements show that introduction of a nitro group does not give rise to substantial furan ring frequency shifts from what obtains with an unsubstituted furan ring, as can be seen from the following figures: furan 1381, 1496, 1576 cm^{-1} ; 2-nitrofurans 1399, 1471, 1574 cm^{-1} .

For all the furan derivatives which we studied, these limits lie inside the limits 1380-1404, 1461-1510 and 1562-1604 cm^{-1} (see Table 1). It is evident that shift of ring vibration frequencies is quite small compared with the corresponding values for furan, indicating the relative "autonomy" of the system of bonds, compared with the behavior of aromatic rings. Evidently some aromaticity, though quite relative, is inherent in the furan ring. In this connection the results obtained for an intermediate nitration product of furfuraldiacetate, 5-nitro-2-acetoxy-2,5-dihydrofurfuraldiacetate (II) are of interest. The structural formula of compound II shows that here one is dealing with the clearly non-aromatic 5-membered ring of dihydrofuran. The spectrum of II well exhibits the C-O-C vibration bands with frequencies 1252 and 1010 cm^{-1} . The other frequencies, belonging to ring vibrations, are markedly displaced, and difficult to identify. This indicates that in the cases of derivatives of furan and 2,5-dihydrofuran, the C-O-C group in any case preserves its separateness, so that it is necessary to speak with care regarding equalization of bonds and aromaticity of the furan ring.



C=C bond vibrations. As soon as the first vinylidene groups appear in the molecules of the compound under investigation, additional bands are found in the 1612-1654 cm^{-1} region (see Table 1). With the majority of compounds these bands are in the region of somewhat lower frequencies than the 1642 cm^{-1} band,

Table 1
Vibration Frequencies for the Furan Ring and C=C Bond in the Side Chain of
Type I Compounds

x.	n	Furan ring vibrations, cm ⁻¹			Pulsating (breathing) vibrations cm ⁻¹	=C—O—C= bond vibrations, cm ⁻¹		—C=C— bond vibrations, cm ⁻¹
		3	4	5		sym	antisym	
1	2	3	4	5	6	7	8	9
H	0	1399	1471	1574	995	1010	1248	—
CHO	0	—	1488	1575	994	1026	1248	—
	1	1394	1472	1567	982	1017	1256	1632
	2	1397	1471	1564	1001	1023	1248	1613
	3	1388	1465	1585	991	1030	1250	1618
COCH ₃	0	1395	1481	1574	980	1038	1261	—
	1	1393	1470	1562	989	1026	1242	1619
	2	—	—	—	—	—	—	—
	3	1404	1465	1588	994	1015	1247	1621; 1638
COOH	0	1384	1504	1588	—	1026	1248	—
	1	1396	1484	1575	1013	1030	1247	1632
COOCH ₃	0	1381	1497	1583	985	1033	—	—
	1	1389	—	1577	1005	1030	1264	1635
COOC ₂ H ₅	0	1402	1471	1582	1012	1027	—	—
	1	1404	1478	1568	983	1021	1243	1637
	2	1390	1468	—	1000	1020	1244	1619
	3	1396	1467	1592	999	1021	1241	1627
	4	1395	1467	1575	998	1021	1243	1622
CH=NNHCOCH ₂ CN	0	1396	1481	1580	1002	1023	1257	—
	1	1392	1467	1595	995	1021	1260	1623
	2	1394	1466	1574	1002	1018	—	1620
	3	1389	1461	—	1003	1022	1251	1620
CH=NNHCSNH ₂	0	1393	1505	1593	976 (?)	1029	1258	—
	1	1395	1500	1583	976 (?)	1025	1259	1612
	2	1393	1487	—	984	1026	1234	1617
	3	1391	1497	1600	998	1026	1241	1617
CH(OCOCH ₃) ₂	0	1399	1510	1604	981	1026	1242	—
	1	1384	1482	1570 (?)	1006	1034	1248	1654
	2	1390	1478	1564	996	1022	1248	1626
Frequency limits	—	1380—	1461—	1562—	976—	1010—	1234—	1612—
		1404	1510	1604	1012	1038	1264	1654

Table 2
=C—O—C= and C—H Vibration Frequencies for Furan, 2-Methyl-
furan, 2-Nitrofuran, and 5-Nitro-2-methylfuran

Group vibrations	Furan	2-Methyl- furan	2-Nitro- furan	5-Nitro-2- methylfuran
=C—O—C= (antisymmetric)	1180	1233	1248	1249
=C—O—C= (symmetric)	997	1015	1010	1030
C—H (deformation)	873	888	878	—

found by Han [16–18], and also by Sobolev, Aleksanyan, and others [19] with vinylfuran, but the manifestation of these bands in the 1600–1650 cm^{-1} frequency range is sufficient to ascribe them to vinylidene groups.

A number of authors note the splitting of the $\text{C}=\text{C}$ group vibration band with more highly conjugated olefins. In our case it was found only for some of the compounds, e.g., 1-(5'-nitrofuryl-2')-1,3,5-octatriene-7-one (I, $\text{X} = \text{COMe}$; $n = 3$).

The intensity of the $\text{C}=\text{C}$ vibration band is rather high, and this is understandable, in view of the clearly asymmetric character of the compounds under investigation. Obviously conjugation with the furan group plays some part in the increase of this band. A similar phenomenon of increase in intensity of this band was observed previously in the case of conjugation of the $\text{C}=\text{C}$ group with a phenyl group [35].

Nitro group vibrations. The nitro group vibrations are of considerable interest for elucidation of the effects of intramolecular interaction in the molecules under investigation. In the type I compounds [20] studied by us, it is para to the position 2 polyene chain, and it offers a possibility of uncovering intramolecular interaction effects, realized through the furan ring. It is known from the literature [21, 22] that conjugation of a nitro group with a double bond results in lowering of the group's antisymmetric vibration frequency. Conjugation with an electronegative group raises the frequency. The same effect is exhibited by electronegative groups in the para position in aromatic compounds [23]. There are no unequivocal data for the frequencies of symmetric vibrations of the nitro group. The above-mentioned effects of displacement of frequencies of antisymmetric vibrations of the nitro group were well observed with the materials studied, while symmetric vibrations of the nitro group were a considerably weaker indicator of the various intramolecular interactions.

Table 3 gives nitro group vibration frequencies with the group at position 5 in the furan ring, with various substituents X at position 2.

Here a rather well-defined regularity is observed. The frequency of the nitro group symmetric vibrations reveals a low sensitivity to the effect of lengthening the conjugated chain in the system of the substituent X. In individual cases there is feeble manifestation of a tendency to a certain raising of the frequency. Simultaneously there is observed an appreciable decrease in frequency of nitro group antisymmetric vibrations. It is characteristic that the maximum frequency lowering corresponds to transition from the starting compound to the first vinylog. Here the value of the jump in frequencies even reaches 29 cm^{-1} , while with further vinylogs the frequency displacement is less, and even tends to a certain saturation. A somewhat anomalous course for the change in frequencies of vibrations of the nitro group is observed with substituents containing the thiosemicarbazido group.

The effect of the relatively great change in frequency of antisymmetric vibrations of the nitro group

under the influence of substituents with different electron-accepting properties, was investigated and interpreted by Bobovich [24]. According to his interpretation, this effect is connected with the gradual equalizing of the $\text{N}=\text{O}$ and $\text{C}=\text{N}$ bonds as the electron-donating capacities of the substituent groups fall off, and the vibrations of the NO_2 group are brought into prominence. Here it is appropriate to recall that with Raman spectra, it is just the symmetric vibrations of the nitro group which are sensitive indicators of intramolecular effects, judging by band intensity, as Shorygin and Ivanova [25], and Bobovich and Perekalin [26] showed; regarding the case of 5-nitrofuran, see [9].

As for symmetric vibrations of the nitro group, though they are also sensitive to intramolecular interaction effects in infrared absorption, their bands are considerably more difficult to interpret. Daasch [12] states that frequencies of the symmetric vibrations of the nitro group are comparatively stable in infrared absorption spectra.

It is quite interesting to note that in the absence of conjugation of the nitro group with multiple bonds, e.g., in the case of 5-nitro-2-acetoxy-2,5-dihydrofurfuraldiacetate (II), and methyl 5-nitro-2-acetoxy-2,5-dihydrofuran-2-carboxylate (III), the IR spectra frequencies not only of the symmetric, but also of the antisymmetric vibrations, appear at considerably higher frequency values (1573–1574 and 1375–1376 cm^{-1}). But here the frequencies of the symmetric vibrations of the nitro group are constrained to considerably smaller shifts than the corresponding antisymmetric vibrations.

Carbonyl group vibrations. The carbonyl group is present in a considerable number of the substituents X of the compounds investigated, so its behavior can to some extent function as an indicator of various intramolecular interactions. It can be connected with the effect of the immediate environment inside the group X, the effect of the system of conjugated $\text{C}=\text{C}$ bonds, and finally, with the effect of the furan ring and nitro group at position 5.

Carbonyl group vibrations are studied in a large number of papers. A detailed study of the effect of the ketone carbonyl group in furan compounds has been made by Lavrushin and coworkers [29–32].

The present work studies the frequency characteristics of the carbonyl group, in the following substituents X of the 5-nitrofurans under consideration: aldehyde, ketone, carboxyl, ester, and acylhydrazone groups (see Table 4).

The following results were obtained as a result of a study of the effect of immediate environment on the frequency of vibrations of the carbonyl group.

Aldehydes ($\text{X} = \text{CHO}$). The initial compound 5-nitrofurfural, gives a carbonyl bond at 1693 cm^{-1} . That is somewhat above the value found by Blout [33] for crotonaldehyde (1685 cm^{-1}). It is curious to note that $\nu_{\text{C}=\text{O}}$ for furfural is equal to 1675 cm^{-1} , i.e., in a frequencies region noted by Blout for polyenaldehydes containing two conjugated ethylenic bonds. It is evident that introduction of a nitro group at position

Table 3
Frequencies of Symmetric (ν^s) and Antisymmetric (ν^{as}) Vibrations of the Nitro Group

Compound	$\nu^s_{NO_2}, \text{ cm}^{-1}$					$\nu^{as}_{NO_2}, \text{ cm}^{-1}$					
	n					n					
	0	1	2	3	4	0	1	2	3	4	
I, X=	H	1357	—	—	—	—	1517	—	—	—	—
	CHO	1354	1354	1354	1369	—	1536	1521	1516	1497	—
	CH(OCOCH ₃) ₂	1338	1345	1353	—	—	1542	1511	1502	—	—
	COCH ₃	1349	1345	—	1340	1348	1532	1521	1516	1511	1506
	COOH	1359	1355	—	—	—	1545	1516	—	—	—
	COOCH ₃	1359	1361	—	—	—	1527	1516	—	—	—
	COOC ₂ H ₅	1356	1353	1354	1356	1358	1530	1515	1509	1508	1509
	CH=NNHCOCH ₂ CN	1354	1351	1345	1356	—	1526	1505	1508	1498	—
II	CH=NNHCSNH ₂	1354	1355	1354	1355	—	1538	1505	1536	1526	—
	—	1376	—	—	—	—	1574	—	—	—	—
III	—	1375	—	—	—	—	1573	—	—	—	—

Table 4
Carbonyl Group Vibration Frequencies in Compounds* R-(CH=CH)_n-X

R	X	$\nu_{C=O}, \text{ cm}^{-1}$				
		$n=0$	$n=1$	$n=2$	$n=3$	$n=4$
5-Nitrofuryl-2	CHO	1693	1678	1672	1664	—
Furyl-2	CHO	1675	—	—	—	—
5-Nitrofuryl-2	COCH ₃	1688	1693	—	1647	1657
Furyl-2	COCH ₃	1688	—	—	—	—
5-Nitrofuryl-2	COOH	1693	1685	—	—	—
Furyl-2	COOH	1682	1663	—	—	—
5-Nitrofuryl-2	COOCH ₃	1728	1702	—	—	—
5-Nitrofuryl-2	COOC ₂ H ₅	1728	1706	1705	1707	1705
5-Nitrofuryl-2	CH(OCOCH ₃) ₂	1762	1772; 1748	1758	—	—
5-Nitrofuryl-2	CH=NHCOCH ₂ CN	1688	1692	1684	1677	—

*For Compound II, $\nu_{C=O}$ is 1772 cm^{-1} .

5 raises the frequency of the carbonyl absorption; this will be considered later.

Introduction of one, two or three vinylidene groups into the chain at position 2 in 5-nitrofuryl-2-polyen-aldehydes lowers the frequency of carbonyl group vibrations by, respectively, 15, 6, and 8 cm^{-1} . Thus in the case of 7-(5'-nitrofuryl-2')-2, 4, 6-heptatrienal (I, $n = 3$, $X = \text{CHO}$), the frequency attains a value of 1664 cm^{-1} . According to Blout's data, this value corresponds to ν_{CO} of 2, 4, 6, 8, 10-undecapentaenal, in good accord with the quasi-diene nature of the furan ring. Apart from the effect of conjugation on carbonyl group frequencies of vibration, the following fact is of interest: The system of bonds of the furan ring is equivalent, for example, to the two conjugated ethylenic bonds in an aliphatic aldehyde. It also holds in a whole series of other cases both for vibration and electronic spectra [8, 9].

In such an interpretation of the system of double bonds of the furan ring, the experimental data for carbonyl group vibration frequencies obtained in the present work agree well with those given in the literature.

Ketones. In the present work, 5-nitrofuryl-2-polyalkenones ($X = \text{COCH}_3$) were investigated. The measurement data show clearly the effect of the immediate neighborhood on the frequency of vibrations of the carbonyl group. However, with the ketones considered, the picture is altogether unique. With the lower members of the 5-nitro-2-acetylfuran series ($R = 5\text{-nitrofuryl-2}$; $n = 0$), as well as with 2-acetylfuran ($R = \text{furyl-2}$; $n = 0$), carbonyl absorption is found at 1688 cm^{-1} , corresponding to a value, found in previously published papers [29-32] for furylketones and α, β unsaturated ketones. Introduction of the double bond $\text{CH}=\text{CH}$ at position 2 not only does not cause lowering of the frequency, as expected, but even gives rise to some increase, to 1693 cm^{-1} . Three conjugated vinylidene bonds lead to a substantial decrease in frequency, to 1647 cm^{-1} , while a fourth gives a fresh increase. It is difficult to interpret this behavior without additional research.

Carboxylic acids ($X = \text{COOH}$). According to data given by Flett [34] and Bellamy [35], carbonyl group absorption is observed in the 1725-1705 region, i. e. in the region where saturated aliphatic ketones also absorb. According to Flett [34], the frequency of absorption of the carbonyl group in α, β -carboxylic acids lies in the 1710-1700 cm^{-1} region. Further conjugation has only a slight effect on this frequency. An aryl group has a more powerful lowering action on ν_{CO} . In this case the latter frequency is found in the 1700-1680 cm^{-1} region. It is of interest to know that this agrees with the value found in the present work, for 2-furancarboxylic acid ($R = \text{furyl-2}$; $n = 0$), i. e. 1682 cm^{-1} . At the same time it is noteworthy that introduction of a vinylidene group between the furan ring and the carboxyl group ($R = \text{furyl-2}$, $n = 1$) substantially affects ν_{CO} , lowering this frequency to 1663 cm^{-1} , a difference from Flett's results [14], which did not show a lowering of these frequencies

when the length of the chain of α, β -unsaturated aliphatic carboxylic acids was increased.

The comparatively low value for the frequency of the vibrations of the carbonyl group in the carboxylic acids considered in the present paper can hardly be ascribed to furan ring "aromaticity," i. e. can hardly be interpreted as due to aromatic substitution. As Freeman [36], and some other authors [37, 38] show, carbonyl group absorption is found in the 1700-1680 cm^{-1} region, and with some α, β -unsaturated aliphatic carboxylic acids too.

Introduction of a $\text{C}=\text{C}$ bond into 5-nitrofuran-2-carboxylic acid causes only an insignificant decrease in carbonyl group frequency (7 cm^{-1}), unlike the 19 cm^{-1} observed with 2-furancarboxylic acid.

Esters of carboxylic acids ($X = \text{COOMe}$; COOEt). Thompson and Torkington's [39] results show that esters of carboxylic acids of saturated compounds absorb near 1740 cm^{-1} . These results agree, for example with those obtained by Jones and coworkers [40-42], and Bellamy [35]. When there is α, β unsaturation, frequency lowering is observed, as has been shown by numerous investigators, e. g. [38, 39, 41, 43]. Further introduction of vinylidene groups is really without appreciable effect [44].

As Table 4 shows, the results of the present research are in good agreement with those given in the literature for esters of 5-nitrofuryl-2-polyene carboxylic acids.

The carbonyl group vibrations frequencies obtained in the present work for esters are somewhat lower than those given in the cited papers of Thompson and coworkers, and closer to the values for α, β unsaturated esters, in close agreement with the above considerations relating to the nature of the furan ring. After lowering of ν_{CO} by, for example, 20 cm^{-1} in the case of the first vinyllog, the frequency of the carbonyl group vibrations is stabilized at a value of about 1705 cm^{-1} , and becomes insensitive to further lengthening of the conjugated chain of $\text{C}=\text{C}$ bonds.

Diacetates [$X = \text{CH}(\text{OAc})_2$]. Compounds of this series are noteworthy on account of the altogether high values of the frequency of the carbonyl group (see Table 4). In these compounds the carbonyl group is completely isolated, both from the system of ethylenic bonds, and from the ring. Here the effect of these groups cannot affect the frequency of the vibrations of the carbonyl group, which also explains the comparatively high value of ν_{CO} . Here we can consider the case of the carbonyl group as analogous to that cited in the literature for the system $\begin{array}{c} >\text{C}-\text{O} \\ | \\ -\text{CH}_2-\text{CH}_2-\text{C}- \\ || \\ \text{O} \end{array}$ [46]. There the frequency of the carbonyl group vibrations can be quite high, and comparable with the values found for diacetates.

Compounds containing the hydrazone group. Among compounds of this class, the family of 5-nitrofuryl-2-cyanoacetylhydrazones was studied. Table 4 gives the relevant measurement data.

Here for example the values of the frequency of the vibrations of the carbonyl group are 40 cm^{-1}

higher than for ordinary N-substituted amides. Obviously here the system $\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-$ has a decisive

effect on the value of this frequency. Actually, as Richards and Thompson showed [45], the frequencies of the vibrations of the carbonyl group in open chain N-substituted amides with an electrophilic substituent on the nitrogen atom can absorb in the 1680 cm^{-1} region, as found in the present work.

Effect of the 5-nitro group on carbonyl group vibrations in the chain of the substituent X. Basically the preceding sections of the present paper considered problems of the effect of immediate environment of the carbonyl group on the frequency of its vibrations in 2-substituted 5-nitrofurans. However, for solution of the problem of intramolecular interaction in molecules of 5-nitrofurans, it would have been extremely interesting to establish such interaction for a nitro group more remote from the carbonyl. In accordance with the strongly electron-accepting properties of the nitro group, conjugation with the latter should have an enhancing effect on ν_{CO} .

To investigate this problem, comparison was made of the spectra of the 2-substituted furans available to us, with those of the corresponding 5-nitro-2-substituted furans. It proved possible to carry out such a comparison for ketones, aldehydes, and carboxylic acids (see Table 4).

It is found that in the case of aldehydes ($\text{X} = \text{CHO}$) and carboxylic acids ($\text{X} = \text{COOH}$), a frequency shift for carbonyl group vibrations in the direction of increased frequency is found when a nitro group is introduced at position 5 in the furan ring. In the case of carboxylic acids the increase in frequency is more clearly marked for the vinylog than in the case of the starting compound, and the increase in frequency here amounts to 22 cm^{-1} .

Regarding ketones, ($\text{X} = \text{COMe}$), there, as with a furyl-2 derivative and with a 5-nitrofuryl-2-one, the same frequency of vibration for the carbonyl group is found, 1688 cm^{-1} . Obviously such stability is rather characteristic of ketones. A similar effect has been pointed out in previous papers [29-32].

Summing up, the presence of quite powerful effects due to near and remote intramolecular interaction are confirmed for 5-nitrofuryl-2-polyalkenes investigated. Both the system of conjugated double bonds and the furan ring system of bonds are quite active transmitters of intramolecular interactions. The present paper shows that the furan ring system of double bonds closely resembles an aliphatic diene system, and which can be regarded as favoring the view that the aromaticity of the furan ring is quite nominal. It is known that similar view flow from a whole series of other observations, of physical and chemical nature, as well as from results of researches on ultraviolet and Raman spectra [8, 9].

EXPERIMENTAL

IR spectra in the $700-1800\text{ cm}^{-1}$ region were recorded with UR-10 and IKS-14 2-beam IR spectro-

eters. Specimens of the compounds, carefully purified, were made into vaseline mulls; for $1300-1500\text{ cm}^{-1}$ mulls with hexachlorobutadiene were used.

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