ether, and the mixture was allowed to stand in a refrigerator for 24 h. The precipitate was removed by filtration to give 0.9 g (8.7%) of γ-(p-nitrophenyl)aminobutyric acid p-nitrophenylanilide with mp 207-209°C (from DMF). Found %: C 55.7; H 4.6; N 16.3. $C_{16}H_{16}N_4O_5$. Calculated %: C 55.8; H 4.7; N 16.3.

2-Phenyliminotetrahydrofuran (IVa). A mixture of 5 g (31 mmole) of orthoester II and 2.5 g (27 mmole) of aniline was refluxed (with removal of the liberated alcohol) for 2 h, after which it was distilled to give 2.9 g (67%) of imido ester IVa with bp 175-176°C (2 mm). Found %: C 74.3; H 7.0; N 8.7. $C_{10}H_{11}NO$. Calculated %: C 74.5; H 6.8; N 8.7.

Imido esters IVb-g were similarly obtained (Table 2).

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^{14}N AND ^{15}N NMR SPECTRA OF 2-SUBSTITUTED 5-NITROFURANS

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UDC 547.722.5'724:543.422.25.4:542.958

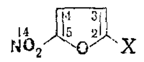
The ^{14}N and ^{15}N NMR spectra of a number of 2-substituted 5-nitrofurans were studied. On the basis of experimental data it was concluded that there is considerable π-electron density on the nitrogen atom of the nitro group. A linear relationship between the chemical shifts in the ^{14}N NMR spectra and the frequencies of the asymmetrical deformation vibrations of the nitro group in the IR spectra was found for the series of investigated 5-nitrofurans. The observed ^{15}N–H spin–spin coupling constants showed that in the 5-nitrofuran molecule transmission of spin information through the ring oxygen atom to the H_2 nucleus is appreciably greater than through the carbon atom to the H_4 nucleus. It was established by measurement of the ^{15}N NMR spectra that the crude adduct formed in the nitration of furfural diacetate with acetyl nitrate is a mixture of trans and cis isomers of 5-nitro-2-acetoxy-2,5-dihydrofurfural diacetate in a ratio of 7:1.

In recent years ^{14}N and ^{15}N NMR spectroscopy has been successfully used for the study of the electronic effects in organic molecules, as well as for the identification of individual compounds; nevertheless, its possibilities as applied to individual classes of compounds have not been fully ascertained. In the present research we were able for the first time to record the ^{14}N and ^{15}N NMR spectra of 2-substituted 5-nitrofurans.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 741-743, June, 1980. Original article submitted November 12, 1979.

0009-3122/80/1606-0568$07.50

TABLE 1. Parameters of the ^{14}N NMR Spectra and IR Spectra of 2-Substituted 5-Nitrofurans

Compound		$\delta(^{14}N)$ (±1), ppm	$\Delta\nu$*, Hz	$\nu^{as}_{NO_2}$, cm^{-1}†
I	X=H	−28,3	70	1536
II	$X=CH_3$	−29,6	70	1540
III	X=CN	−31,1	70	1548
IV	X=CHO	−28.8	92	1533
V	$X=COCH_3$	−29,7	84	1542
VI	$X=CF_3$	−31,0	90	1565
VII	$X=COOCH_3$	−28,6	80	1535
VIII	X=I	−27,3	80	1511

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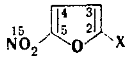
*Half-width of the line (± 5 Hz).

†The $\nu^{as}_{NO_2}$ value was determined with an accuracy of ± 2 cm^{-1}.

TABLE 2. Chemical Shifts and Spin—Spin Coupling Constants (SSCC) with Participation of the ^{15}N Nucleus in Nitrofuran Derivatives

Compound		$\delta(^{15}N)$, ppm (± 0.3)	SSCC, J, Hz (±0.1)						
			$^{15}N—H_3$	$^{15}N—H_4$	$^{15}N—H_2$	$^{15}N—C_4$	$^{15}N—C_3$	$^{15}N—C_2$	$^{15}N—C_5$
I	X=H	−27,7	0,4	0	0,7	3,2	1,8	1,5	26,6
IX	$X=CH(OCOCH_3)_2$	−28,7	0,4	0	—	3,5	1,8	1,8	27,2
X	$X=CH=NNHCONH_2$	−28,3	0,2	0	—	—	—	—	—

2-Substituted 5-nitrofurans can be formally regarded as analogs of p-substituted nitrobenzenes. In fact, the half-width of the absorption lines of the ^{14}N nucleus that is characteristic for nitrofurans (Table 1) was found to be extremely close to that in the spectra of nitrobenzenes (80-100 Hz) [1]. At the same time, the ^{14}N resonance of the nitro group in nitrofurans, as in 2-nitropyrrole [$\delta(^{14}N)$ = −22.5 ppm [2]], appears at considerably stronger field than in the case of the corresponding nitrobenzenes [$\delta(^{14}N)$ = −6 to −13 ppm [3]]. A linear correlation between the ^{14}N chemical shifts and the π-electron density on the nitrogen atom was recently found for nitrogen heterocycles [4]. It may therefore be assumed that the more negative $\delta(^{14}N)$ values for the nitro group in nitrofurans as compared with the nitro group in nitrobenzenes reflect precisely the increased π-electron density on the nitrogen atom. This conclusion is in agreement with the results of quantum-chemical calculations [5].

It is apparent from the data in Table 1 that the ^{14}N chemical shifts in the spectra of 2-substituted 5-nitrofurans depend only slightly on the electronic effects of the substituents. A similar phenomenon was also observed for substituted nitrobenzenes [3] and nitropyrroles [2]. It was noted that this is associated with the insensitivity of the ^{14}N resonance in the nitro group to the effects of conjugation [2]. Unfortunately, the accuracy in the measurement of the ^{14}N chemical shifts at a line width of 70-90 Hz and a frequency of 6.5 MHz is not sufficient for verification of this assumption.

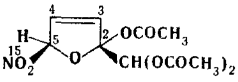
We compared the ^{14}N chemical shifts with the frequencies of the asymmetrical deformation vibrations of the nitro group in the IR spectra. Although the literature contains individual values for these frequencies [7, 8], for a complete comparison we conducted a new spectroscopic investigation of them. A linear relationship between these values was found:

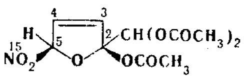
$$\delta(^{14}N) = 91.68 - 0.008\nu_{NO_2}{}^{as};\ S = 1.54;\ r = 0{,}91.$$

This result constitutes evidence for a dependence of the shielding constant of the ^{14}N nucleus in the nitro group on the force constant of the N—O bond. Since the latter is determined by the bond order, it may be assumed that the ^{14}N chemical shifts in the spectra of nitrofurans depend primarily on the order of the N—O bond.

We also synthesized and investigated some ^{15}N-labeled nitrofurans and studied their ^{15}N NMR spectra (Table 2). The observed ^{15}N—H spin—spin coupling constants through four bonds are larger in absolute value than those through three bonds. The transmission of spin information through the ring oxygen atom to the H_2 nucleus is appreciably greater than through the carbon atom to the H_4 nucleus.

The ^{15}N NMR spectra also made it possible to introduce additional information regarding the structure of the "intermediate" in the nitration of furfural and furfural diacetate. It has been previously shown that the product (mp 109.0-110.5°C) of the addition of acetyl nitrate to furfural diacetate has trans-adduct structure XIa [9]. The measurements made in this research established that the crude product (mp 97-102°C) formed in the nitration of furfural diacetate also contains a small amount of a second isomer, i.e., it is a mixture of trans and cis isomers XIa and XIb in a ratio of 7:1.


XIa


XIb

XIa δ (^{15}N) = 5,8 ppm, $J\ ^{15}N—H_3 = 0$ Hz, $J\ ^{15}N—H_4 = 0{,}6$ Hz, $J\ ^{15}N—H_5 = 1{,}3$ Hz $J\ ^{15}N—C_4 = 0$ Hz $J\ ^{15}N—C_3 = 0$ Hz $J\ ^{15}N—C_2 = 0$ Hz, $J\ ^{15}N—C_5 = 8{,}8$ Hz; XIb δ (^{15}N) = 7,6 ppm.

A study of the NMR spectra of labeled XIa made it possible to interpret the ^1H spectrum for the protons of the 2,5-dihydrofuran ring more reliably than in [10]. The refined chemical shifts are H_3 = 6.73, H_4 = 6.56, and H_5 = 6.62 ppm.

EXPERIMENTAL

The ^{14}N and ^{15}N NMR spectra were obtained with a WH-90/DS spectrometer under pulse conditions. The pulse duration corresponded to 30°C rotation of the magnetization vector (11 μsec). The time interval between the pulses was 5 sec for the ^{15}N nuclei. The chemical shifts were measured relative to nitromethane as the external standard for solutions in d_6-DMSO (30% for ^{14}N and 5% for ^{15}N). The average number of build-ups was 3000, and the sample temperature was 30°C. The IR spectra of suspensions of the compounds in Nujol were obtained with a UR-20 spectrometer.

2-^{15}N-Nitrofuran- (I) and 5-^{15}N-nitro-2-furfural diacetate (IX) were obtained by nitration of the corresponding furan compounds in acetic anhydride as in [11] (the molar ratio of the furan compound, ^{15}N-nitric acid, and acetic acid was 1:1.2:9). The nitrating agent was prepared by slow addition of the calculated amount of 48% nitric acid (containing 99% of the ^{15}N isotope) to acetic anhydride at 0 to 10°C with subsequent standing of the resulting solution at the same temperature for 45 min. Compound IX was synthesized from furfural in the presence of catalytic amounts of concentrated sulfuric acid (0.04 mole per mole of starting furfural). The adduct formed in this reaction, viz., 5-^{15}N-nitro-2-acetoxy-2,5-dihydrofurfural diacetate (XI), was isolated from the reaction mixture by the method in [12] by dilution of the reaction mixture with excess cold water. 5-^{15}N-Nitro-2-furfurylidenesemicarbazide (X) was obtained from IX by the method in [13]. The 2-substituted 5-^{14}N-nitrofurans were obtained by known methods. Their constants were in agreement with the literature data [14-16].

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THREE-DIMENSIONAL STRUCTURES OF DIHYDROPYRANS

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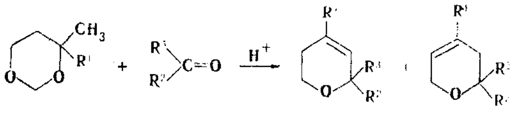
UDC 541.63:547.811:543.422.25

The three-dimensional structures of alkyl- and aryldihydropyrans were studied by means of PMR spectroscopy. It is shown that the investigated compounds exist primarily in the half-chair conformation.

Six-membered saturated and unsaturated heterocycles constitute the prevalent fragments of natural and biologically active compounds and in many respects determine their structures and properties. Owing to the presence of an unsaturated bond in the ring, dihydropyrans are, in addition, convenient substrates for the synthesis of analogs of natural compounds. However, the literature does not contain information regarding the determination of the position of the double bond by NMR methods, the spin–spin coupling constants (SSCC), the effect of substituents on the conformations, etc.

We synthesized alkyl- and aryl-substituted dihydropyrans I and II by the reaction of 4, 4-dimethyl- and 4-methyl-4-phenyl-1,3-dioxanes with aldehydes and ketones:



I-II a, IV-VI a, IX-XII a   I-VIII b, Xb, XII b

I $R^1=C_6H_5$, $R^2=R^3=H$; II $R^1=C_6H_5$, $R^2=H$, $R^3=i\text{-}C_3H_7$; III $R^1=C_6H_5$, $R^2=H$, $R^3=n\text{-}C_4H_9$; IV $R^1=C_6H_5$, $R^2=CH_3$, $R^3=C_2H_5$; V $R^1=CH_3$, $R^2=R^3=H$; VI $R^1=CH_3$, $R^2=H$, $R^3=i\text{-}C_3H_7$; VII $R^1=CH_3$, $R^2=H$, $R^3=n\text{-}C_4H_9$; VIII $R^1=CH_3$, $R^2=H$, $R^3=C_6H_5$; IX $R^1=CH_3$, $R^2=R^3=C_2H_5$; X $R^1=CH_3$, $R^2=CH_3$, $R^3=C_2H_5$; XI $R^1=CH_3$, $R^2=CH_3$, $R^3=n\text{-}C_3H_7$; XII $R^1=CH_3$, $R^2=CH_3$, $R^3=n\text{-}C_4H_9$

The three-dimensional structures of these compounds were studied by PMR spectroscopy. The SSCC were determined by means of double homonuclear resonance. The chemical shift and the structure of the signal of the 6-H methylene protons are most informative for the determination of the position of the double bond in the ring (Table 1). In the case of 4-methyl-5,6-dihydro-2H-pyran (Va) the 6-H signal is a triplet with δ 3.60 ppm and $^3J_{65}$ = 5.5 Hz. The absence of geminal splitting of the 5- and 6-H methylene protons constitutes evidence for their equivalence. This is possibly a consequence of rapid (on the NMR time scale) ring inversion. The 5-H protons in 2-substituted dihydropyrans Xa-XIIa are nonequivalent if $R^2 \neq R^3$, and the 6-H signal is a doublet of doublets with $^3J_{5a6}$ = 6.0 Hz and $^3J_{5e6}$ = 4.6 Hz. The $^3J_{56}$ values are virtually independent of the structure of the alkyl substituents attached to C_2. However, if $R^2 = R^3$, the signal of the 5-H protons is simplified to a triplet.

Ufa Petroleum Institute, Ufa 450062. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 744-747, June, 1980. Original article submitted July 23, 1979.

0009-3122/80/1606-0571$07.50