

RESEARCH ON FURAN ACETAL COMPOUNDS

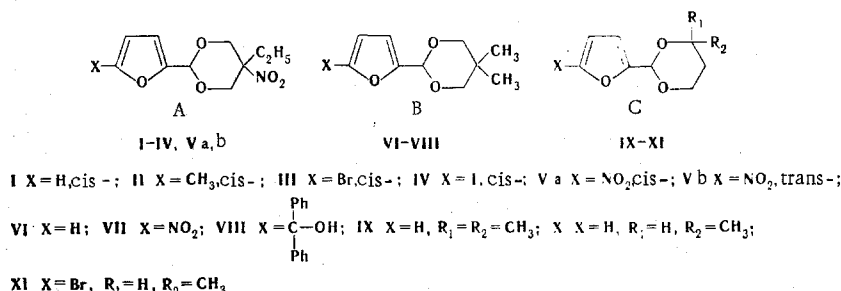
VII.* PMR SPECTRA, CONFIGURATION, AND CONFORMATIONS OF SUBSTITUTED 2-(α -FURYL)-1,3-DIOZANES

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The configuration and preferred conformations of a number of stereoisomeric 2-(α -furyl)-1,3-dioxanes were established by PMR spectroscopy. It is shown that cis orientation of the NO_2 groups with respect to the furyl ring is primarily realized for 2-(α' -nitro- α -furyl)-5-ethyl-5-nitro-1,3-dioxanes.

In order to investigate the stereochemistry of 1,3-dioxanes of the furan series [2], we synthesized α' -substituted 2-(α -furyl)-5-ethyl-5-nitro- (A), α' -substituted 2-(α -furyl)-5,5-dimethyl- (B), and α' -substituted 2-(α -furyl)-4-mono methyl [or 4,4-dimethyl- (C)]-1,3-dioxanes [3, 4].



The present communication is devoted to the proof of the configuration and establishment of the preferred conformations of 1,3-dioxanes of series A, B, and C by PMR spectroscopy.

The proton chemical shifts (δ) and the spin-spin coupling constants ($J_{\text{HH}'}$) of compounds I-XI are summarized in Table 1.

As will be shown below, the preferred chair conformation for the 1,3-dioxane ring is realized in all of the investigated systems, and the methylene protons in the 4 and 6 positions are therefore denoted as H_A (axial) and H_B (equatorial) in Table 1. In a preceding communication [2], it was shown that the relative magnetic nonequivalence of these protons ($\Delta\delta_{\text{AB}}$) may serve as a test sign of both the configuration and the conformation of the 1,3-dioxane system. Inasmuch as proton vicinal spin-spin couplings are absent in series A and B because of the presence of two substituents attached to the C(5) atom, we judge the configuration of the substituents and the conformation of the six-membered heteroring by relying on the theoretically expected relative changes in the nuclear magnetic shielding constants ($\Delta\sigma^2$). These estimates show that in the case of 5,5-dimethyl-1,3-dioxane the H_A and H_B protons for a chair conformation should have great relative nonequivalence ($\Delta\sigma_{\text{AB}}^{\text{th}} \cong 0.8$ ppm), should be practically equivalent for a symmetrical boat conformation ($\Delta\sigma_{\text{AB}}^{\text{th}} \cong 0.004$ ppm), and that the nonequivalence should be small for the unsymmetrical boat conformation ($\Delta\sigma_{\text{AB}}^{\text{th}} \cong 0.14$ ppm for 4- CH_2 and 0.22 ppm for 6- CH_2). Turning to Table 1, we see that the

*See [1] for communication VI.

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TABLE 1. Proton Chemical Shifts (δ) and Spin-Spin Coupling Constants ($J_{HH'}$) of 1,3-Dioxanes of the Furan Series

Com- pound	mp, °C	Chemical shifts, δ , ppm (relative to tetramethylsilane)†											
		H_A	H_B	$\Delta\delta_{AB}$	H_A	C_2H_5		4- CH_3		5- CH_3		$\alpha'-CH_3$	$^2J_{AB}$, Hz‡
						- CH_3	- CH_2	Eq.	Ax.	Eq.	Ax.		
I	57	3.07	4.64	1.57	5.24	0.32	0.92	—	—	—	—	—	-12.6
II	99	3.08	4.68	1.60	5.26	0.32	0.92	—	—	—	—	1.92	-12.3
III	116	2.98	4.60	1.62	5.06	0.32	0.89	—	—	—	—	—	-13.0
IV	125	3.03	5.13	2.10	5.15	0.33	0.92	—	—	—	—	—	-12.7
V _a	139	3.04	4.60	1.56	4.93	0.34	0.93	—	—	—	—	—	-12.7
V _b	107	3.55	3.94	0.39	4.72	0.57	1.84	—	—	—	—	—	-11.5
VI	112 (2)*	3.40	3.57	0.17	5.37	—	—	—	—	0.70	1.21	—	-10.8
VII	109	3.51	3.68	0.17	5.44	—	—	—	—	0.73	1.21	—	-12.0
VIII	94	—	—	—	5.34	—	—	—	—	0.70	1.19	—	—
IX	109 (7)*	—	3.89	—	5.64	—	—	1.30	1.37	—	—	—	—
X	116 (6)*	—	4.00	—	5.45	—	—	1.20	1.30	—	—	—	—
XI	46	—	3.97	—	5.47	—	—	1.24	1.34	—	—	—	—

*Boiling point (mm, mercury standard).

† The chemical shifts (δ) were determined with an accuracy of ± 0.005 ppm.

‡ The $J_{HH'}$ constants were determined with an accuracy of ± 0.1 Hz.

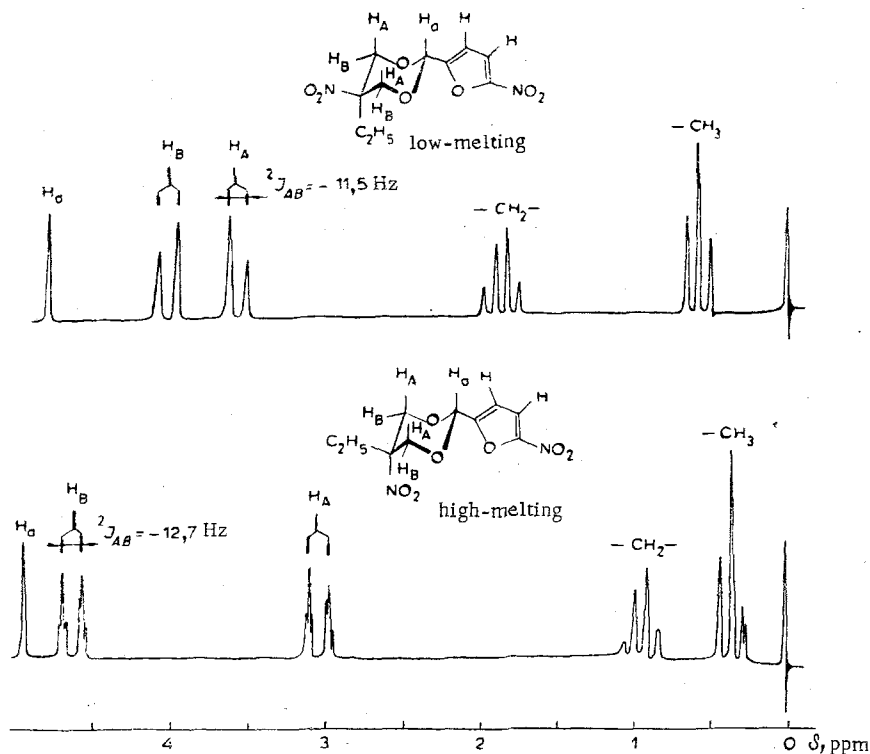


Fig. 1. PMR spectra of 2-(α' -nitro- α -furyl)-5-ethyl-5-nitro-1,3-dioxanes: low-melting isomer (trans form) and high-melting isomer (cis form).

$\Delta\delta_{AB}$ values (column 5) for I-Va considerably exceed the $\Delta\sigma_{AB}^{th} \cong 0.8$ ppm value and range from 1.56 to 2.10 ppm. This fact, first of all, attests to the chair conformation of the 1,3-dioxane ring and, second, indicates an axial conformation of the nitro group, inasmuch as when the nitro group has an equatorial conformation, the experimentally observed $\Delta\delta_{AB}$ value, as shown in [2], corresponds to the estimated $\Delta\sigma_{AB}^{th}$ value. The chemical shifts of the CH_2 and CH_3 groups of the ethyl grouping also indicate the axial orientation of the NO_2 group and, consequently, the equatorial conformation of the ethyl group. The PMR spectra of two stereoisomers of V are presented in Fig. 1. From the lower spectrum, which corresponds to the high-melting isomer, it is seen that the protons of the CH_2 and CH_3 groups resonate at "anomalously" high

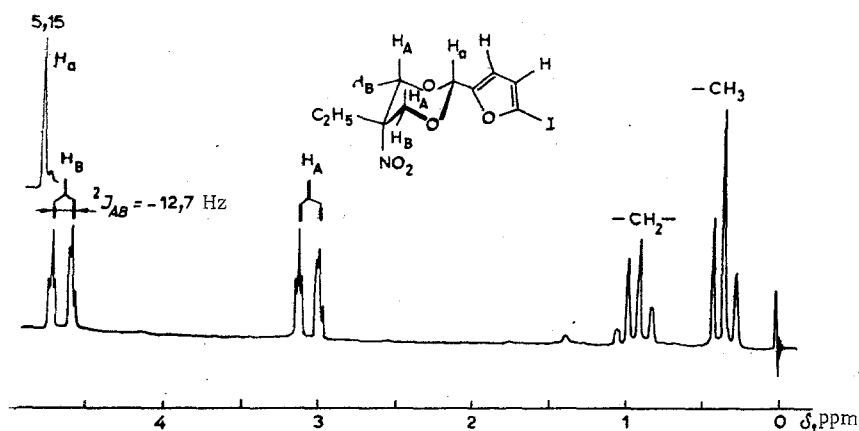


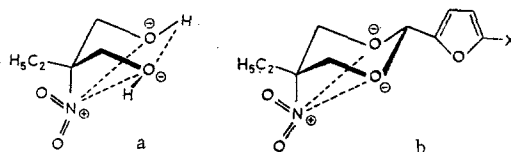
Fig. 2. PMR spectra of 2-(α' -iodo- α -furyl)-5-ethyl-5-nitro-1,3-dioxane.

magnetic field values; this is possible in six-membered cyclic ethers and esters, as shown in a paper by one of the co-authors [5], for an equatorial orientation of, for example, the C_2H_5 group. However, if the ethyl group occupies an axial position, the line of the CH_2 group is shifted to lower field ($\delta = 1.84$ ppm), and the magnitude of the nonequivalence of the H_A and H_B protons decreases to $\Delta\delta = 0.39$ ppm. The equatorial conformation of the furan ring in I-XI can be judged from the magnitude of the chemical shift of the singlet of the proton attached to C(2) [2]; this shift is 4.72–5.70 ppm in all of the investigated compounds.

In general features, the PMR spectra of I-IV duplicate the form of the spectrum of the high-melting stereoisomer Va (Fig. 1), as can be judged from the spectrum of, for example, IV (Fig. 2).

Thus we arrive at the conclusion that the molecules of I-Va have cis orientation of the NO_2 groups with respect to the furyl group, i.e., they can be called cis isomers, while Vb is a trans isomer with diequatorial orientation of the polar substituents. If one considers that the volume of the C_2H_5 group is greater than the volume of the NO_2 group, it can be seen that the stereospecificity of the condensation reactions of diols with aldehydes of the furan series is regulated by the effective volumes of the substituents attached to the C(5) atom rather than by their masses.

In addition, the preferableness of the axial conformation of the nitro group in most of the compounds of series A can be readily understood from a qualitative point of view if one considers that the axial position of the C(5) atom is unique. The fact is that the axial conformation of the nitro group both in the diol itself, in which a quasichair conformation is realized because of intramolecular hydrogen bonding (see the scheme below, conformation a) in the transition state, and, doubtlessly, in the final product should be stabilized by electrostatic interaction (attraction) between the nitrogen atom bearing a positive charge and the endocyclic oxygen atoms (conformation b).



The PMR spectra of compounds of series B contain a radical difference in the character of the resonance of the 4,6- CH_2 groups, which consists in the considerably lesser nonequivalence of the H_A and H_B protons (see Table 1).

It would seem that this indicates a change in the conformation of the 1,3-dioxane ring if the resonance of the protons of the methyl groups of the gem-dimethyl grouping did not have features peculiar to the chair conformation. The spectrum of VII, from which the characteristic difference in the amplitude of the methyl lines is seen, is presented in Fig. 3. This difference is due to the unresolved multiplet structure of the line at lower field. It is known that the shielding constants of the methyl groups attached to C(5) undergo inversion [5] and that consequently the line at weak field must be assigned to the axial methyl group if one adopts the chair conformation. Its additional multiplicity is then understood as a consequence of the long-range spin-spin coupling ($^4J_{HH'}$) with the axial H_A protons of the 4,6- CH_2 groups. This sort of coupling is always realized with a lower $^4J_{HH'}$ constant for an equatorial proton. The magnitudes of the relative nonequivalence

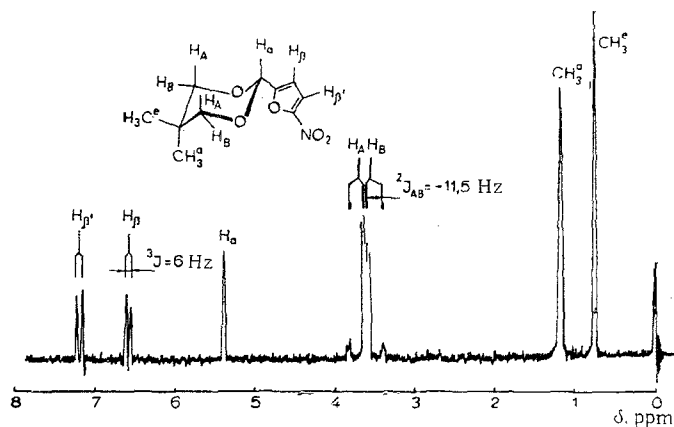


Fig. 3. PMR spectrum of 2-(α' -nitro- α -furyl)-5,5-dimethyl-1,3-dioxane.

of the protons of the gem-dimethyl grouping [$\Delta\delta_{\alpha e}(\text{CH}_3)$ 0.48–0.51 ppm] are typical [5] for the chair conformation in cyclic ethers and esters. However, the reason for the low nonequivalence of the H_A and H_B protons in series B remains unclear and requires further study. It seems premature to consider it to be the result of compression of the chair.

Compounds X and XI in series C may be stereoisomeric, but, according to the PMR spectra, the investigated samples are pure *cis* isomers with diequatorial orientation of the substituents. This can be judged from the lone 4- CH_3 doublets ($J_{\text{HH}'} = 6$ Hz) with chemical shifts $\delta = 1.29$ ppm in both compounds. This sort of shift is characteristic for an equatorial methyl group attached to the C(4) or C(6) atom. Taking into account the possibility of a strong 1,3-interaction of the axial furyl grouping, we assign an equatorial conformation to it.

In conclusion, it must be noted that donor-acceptor substituents in the α -position of the furan ring – CH_3 , I, Br, and NO_2 – have practically no effect on the conformation of the six-membered ring, as can be judged from the absence of definite tendencies in the small changes in the chemical shifts of the protons of the 1,3-dioxane ring.

EXPERIMENTAL

The preparation of the 2-(α -furyl)-1,3-dioxanes studied in this research was described in [1, 3, 4]. The PMR spectra of 5–10 vol. % solutions of I–V in benzene and of 10 vol. % solutions of VI–XI in CCl_4 were recorded with Varian HA-100D and Varian T-60 spectrometers at room temperature. Tetramethylsilane was used as the internal standard.

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