

**¹H- AND ¹³C-NMR STUDY
OF (X-PHENYL)-5-NITRO-2-FURYLVINYL ETHERS***

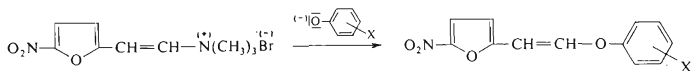
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Reaction of 5-nitro-2-furylvinyltrimethylammonium bromide with substituted phenolates gave (*E*)- and (*Z*)-(X-phenyl)5-nitro-2-furylvinyl ethers. The preferred *s-cis* and *s-trans* orientations of the furan ring in *Z* and *E* isomers, respectively, were determined by ¹H-NMR spectroscopy. To study the extent of *p*- π conjugation, ¹³C-NMR spectra of compounds under investigation have also been measured and interpreted. Chemical shifts for ethylenic carbons and protons were correlated with Hammett σ constants.

With the aim to study the effect of substitution at the terminus of the ethylenic linkage in 5-nitro-2-furylethylenic compounds, the possibilities of preparing a new class of 5-nitrofuran substances, namely (X-phenyl)-5-nitro-2-furylvinyl ethers, has been investigated. Reaction of 5-nitro-2-furylvinyltrimethylammonium bromide¹ with substituted alkali phenolates gave (X-phenyl)-5-nitro-2-furylvinyl ethers in high yields (65–95%) (Scheme 1). Physical constants of the prepared substances are in Table I.



SCHEME 1

Structural and stereochemical information about the prepared substances was obtained by ¹H-NMR spectroscopy. Spectra of mixtures of *E* and *Z* isomers were measured; only in the case of *II* the individual isomers could be separated by crystallization and, thus, spectra of pure isomers were obtained. The observed spectral data are given in Table II. The isomery assignment was based on the magnitude of the found coupling constants for vicinal olefinic protons (12.2–12.4 and 6.6 to 6.8 Hz for *E* and *Z* isomers, respectively).

* Part CLII in the series Furan Derivatives; Part CLI: This Journal 45, 3546 (1980).

In connection with our previous studies on the stereochemistry of furylethylenic derivatives²⁻⁵ we have attempted to determine the arrangement of the furylethylenic system in the synthesized substances. The ¹H-NMR spectra of the pairs of *E* and *Z* isomers show a noticeable difference in the chemical shift of the H₃ proton of the furan ring ($\Delta\delta = 0.47-0.62$). As a result of the deshielding effect of the ether oxy-

TABLE I
Properties of Isomeric Mixtures of (X-Phenyl)5-nitro-2-furylvinyl Ethers

Compound X	Formula (m.w.)	M.p., °C (yield, %)	Calculated/Found		
			% C	% H	% N
<i>I</i>	C ₁₂ H ₉ NO ₄	102—105	62.34	3.92	6.06
H	(231.2)	(85)	62.27	3.86	5.97
<i>II</i>	C ₁₃ H ₁₁ NO ₄	^a	63.67	4.52	5.71
4-CH ₃	(245.2)	(90)	63.60	4.48	5.80
<i>III</i>	C ₁₃ H ₁₁ NO ₄	41—45	63.67	4.52	5.71
2-CH ₃	(245.2)	(70)	63.59	4.46	5.65
<i>IV</i>	C ₁₂ H ₈ ClNO ₄	75—78	54.20	3.03	5.27
4-Cl	(265.6)	(85)	54.07	3.10	5.32
<i>V</i>	C ₁₂ H ₈ ClNO ₄	54—57	54.20	3.03	5.27
2-Cl	(265.6)	(70)	54.08	3.12	5.36
<i>VI</i>	C ₁₂ H ₈ BrNO ₄	112—115	46.50	2.60	4.51
4-Br	(310.1)	(80)	46.38	2.52	4.60
<i>VII</i>	C ₁₂ H ₈ INO ₄	140—142	40.37	2.26	3.92
4-I	(357.1)	(75)	40.28	2.20	3.88
<i>VIII</i>	C ₁₃ H ₈ N ₂ O ₄ S	98—102	54.17	2.80	9.72
4-NCS	(288.2)	(70)	50.06	2.72	9.68
<i>IX</i>	C ₁₅ H ₁₃ NO ₅	101—103	62.71	4.56	4.88
4-COC ₂ H ₅	(287.2)	(80)	62.59	4.51	4.79
<i>X</i>	C ₁₂ H ₈ N ₂ O ₆	128—136	52.18	2.92	10.14
4-NO ₂	(276.2)	(75)	52.07	2.87	10.03
<i>XI</i>	C ₁₂ H ₈ N ₂ O ₆	125—128	52.18	2.92	10.14
3-NO ₂	(276.2)	(70)	52.02	2.90	10.04
<i>XII</i>	C ₁₂ H ₈ N ₂ O ₆	120—125	52.18	2.92	10.14
2-NO ₂	(276.2)	(65)	52.01	2.79	10.01

^a 87—90°C (*E* isomer), 75—78°C (*Z* isomer).

gen atom the signals for H₃ in Z isomers appear downfield, compared with the corresponding E isomers where the same interaction cannot operate. It can be seen from data in Table II that in the pairs of isomers H₄ protons are not influenced either by the position of the substituent on the double bond or by the substitution

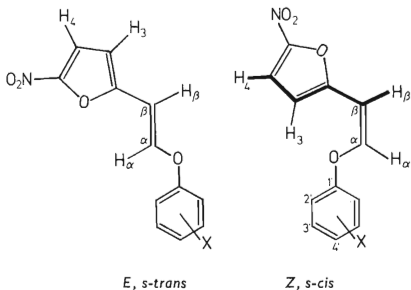
TABLE II
Chemical Shifts (δ , ppm) for Z and E Isomeric Compounds under Investigation

Compound X	Isomer	H _{α} ^a	H _{β} ^a	H ₃ ^b	H ₄ ^b	C _{α}	C _{β}	C ₃	C ₄
I	Z	6.93	5.74	6.92	7.37	147.2	98.0	112.1	114.4
	E	7.56	6.07	6.30	7.29	149.6	99.8	108.5	114.4
II ^c 4-CH ₃	Z	6.87	5.68	6.88	7.32	147.9	97.6	112.1	114.4
	E	7.52	6.01	6.28	7.26	150.2	99.4	108.3	114.4
III 2-CH ₃	Z	6.86	5.69	6.88	7.32	—	—	—	—
	E	7.51	5.93	6.27	7.24	—	—	—	—
IV 4-Cl	Z	6.85	5.77	6.87	7.35	146.6	98.6	112.3	114.2
	E	7.50	6.08	6.32	7.29	148.9	100.5	109.0	114.2
V 2-Cl	Z	6.91	5.83	7.12	7.37	—	—	—	—
	E	7.50	6.05	6.32	7.29	—	—	—	—
VI 4-Br	Z	6.84	5.78	6.87	7.36	146.5	98.6	112.4	114.3
	E	7.51	6.09	6.32	7.30	148.7	100.7	109.1	114.3
VII 4-I	Z	6.86	5.79	6.88	7.37	146.2	98.8	112.3	114.1
	E	7.52	6.10	6.33	7.33	148.5	100.8	109.0	114.1
VIII 4-NCS	Z	6.86	5.81	6.88	7.36	146.1	99.1	112.5	114.2
	E	7.55	6.13	6.35	7.31	148.1	101.2	109.3	114.2
IX 4-COC ₂ H ₅	Z	6.98	5.86	6.90	7.37	145.3	99.5	112.5	114.0
	E	7.62	6.21	6.38	7.33	147.3	101.7	109.3	114.0
X 4-NO ₂	Z	6.96	5.94	6.89	7.36	114.1	100.9	113.0	114.0
	E	7.57	6.29	6.42	7.32	146.1	103.2	110.2	114.0
XI 3-NO ₂	Z	6.96	5.91	6.92	7.38	145.1	100.2	112.8	114.0
	E	7.57	6.24	6.41	7.33	147.2	102.4	109.8	114.0
XII 2-NO ₂	Z	6.90	5.96	7.18	7.39	—	—	—	—
	E	7.54	6.21	6.38	7.37	—	—	—	—

^a $J_{H_{\alpha}, H_{\beta}}$: 6.6—6.8 Hz (Z), 12.3—12.5 Hz (E); ^b J_{H_3, H_4} = 3.9 Hz; ^c ¹³C (δ , ppm): Z isomer — 150.4 (C₅), 153.8 (C₂), 154.6 (C₁), 117.0 (C₂), 130.5 (C₃), 134.4 (C₄), 20.7 (CH₃); E isomer — 151.3 (C₅), 153.9 (C₂), 155.0 (C₁), 117.6 (C₂), 130.5 (C₃), 134.4 (C₄), 20.7 (CH₃).

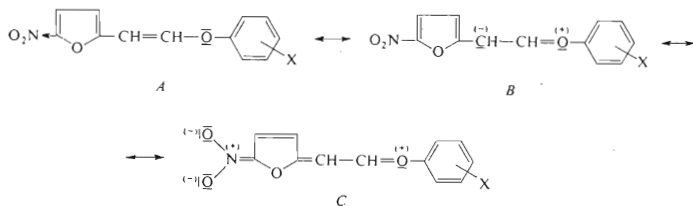
on the phenyl ring. This proves that the downfield shift of the H_3 signal observed with *Z* isomers results exclusively from steric and conformational factors, and indicates their *s-cis* arrangement. Our previous determination²⁻⁵ of the prevalence of the furan ring orientation in similar isomeric substances was based on the observed different chemical shift of the heterocyclic H_3 proton caused by its different chemical environment, and other authors⁶⁻⁹ took advantage of the same phenomenon when studying the conformation of ethylenic five-membered heterocyclic derivatives. The above conclusions are also proved by the fact that compounds *V* and *XII*, bearing strongly deshielding Cl and NO_2 groups in *ortho* position, show chemical shifts for H_3 of the *Z* isomer much further downfield, as compared with the corresponding 4-substituted *Z* isomer. Compound *III* having a methyl group in *ortho* position does not show the same effect.

The determination of the orientation of the furan ring in (*X*-phenyl)5-nitro-2-furylvinyl ethers was based on values of stereospecific long-range coupling constants $^5J_{H,H}$ found for olefinic H_β and H_4 furan-ring protons. Such constants between H_4 and H_5 in a heterocyclic 5-membered ring are normally used for determination of the predominating conformation of related ethylenic substances⁸⁻¹². Owing to the presence of a nitro group in the position 5 of the furan ring in (*X*-phenyl)5-nitro-2-furylvinyl ethers it was impossible to compare $^5J_{H_\beta, H_4}$ and $^5J_{H_\beta, H_3}$ values. However, for the corresponding pairs of *E* and *Z* isomers a large difference of long-range constant values between H_4 of the furan ring and the olefinic H_β proton has been



observed. In *s-cis* conformation there is a five-linkage *W* arrangement across which a rather pronounced interaction can be expected. In the case of *Z* isomers the $^5J_{H_\beta, H_4}$ was 0.7 Hz whereas with *E* isomers this value was either very small or was not observed at all ($^5J_{H_\beta, H_4} \leq 0.2$ Hz). These long-range interactions were proved by decoupling experiments. The high $^5J_{H_\beta, H_4}$ value observed with *Z* isomers supports

the above-mentioned conclusion that *Z* isomers exist in *s-cis* conformation, whereas with *E* isomers the *s-trans* conformation is preferred. Low-temperature (down to -80°C) measurements, run with both isomers, did not show changes in either spectral parameters of the width of lines, indicating the existence of only one conformer. The existence of *s-cis* conformation of the *Z* isomer can be explained by decreased stability of the *s-trans* conformation resulting from electrostatic repulsion between the heterocyclic and ether oxygen atoms.



To investigate the question of the extent of *p*- π conjugation in (*X*-phenyl)5-nitro-2-furylvinyl ethers ^{13}C -NMR spectra of their 4- and 3-substituted derivatives have been measured. Since, except for compound *II*, spectra of isomeric mixtures were measured Table *II* does not contain chemical shifts of all carbon atoms. ^1H - and ^{13}C -NMR spectra made it possible to solve the question concerning the nature and the degree of *p*- π conjugation in substituted phenylvinyl ethers $^{13-15}$ a characteristic feature of which is a high degree of *p*- π conjugation. With the compounds under investigation the *p*- π conjugation can be demonstrated by structures *A*–*C*. The presence of a negative charge at the C_β carbon atom, expected according to the resonance structure *B*, was proved by both ^{13}C - and ^1H -NMR spectroscopy. For comparison ^{13}C - and ^1H -NMR spectra of 5-nitro-2-vinylfuran 16 have also been measured.

TABLE III
Correlations of C_β , C_α and H_β Chemical Shifts with Hammett σ constants ($n = 8$)

Atom	<i>Z</i> Isomer		<i>E</i> Isomer	
	ρ	r	ρ	r
C_β	3.94	0.968	3.28	0.983
C_α	-4.10	0.977	-3.73	0.986
H_β	0.28	0.970	0.26	0.992

They showed that with *e.g.* (*Z*)-phenyl-5-nitro-2-furylvinyl ether the C_β carbon and H_β hydrogen atoms are shielded by 24.9 and 0.8 ppm, respectively, compared with the corresponding atoms in 5-nitro-2-vinylfuran. The results of ^{13}C - and ^1H -NMR measurements show that in compounds under investigation the range of p - π conjugation is largely affected by the character of the substituent at the phenyl ring and that the extent of this conjugation increases with the increasing electron-donating character of the substituent, and *vice versa*. A good linear correlation of ^{13}C chemical shifts for C_β and C_α , as well as of ^1H chemical shifts for H_β , with Hammett σ constants (Table III) has been found. The ^{13}C chemical shifts of α and β carbon atoms are inversely affected by the effects of substituents. The H_α proton chemical shifts are markedly influenced by shielding effects of the phenyl ring which manifested itself by worsened correlation and, hence, these values could not be used as a measure of the extent of polar conjugation. The tangency of the correlation line of C_β carbons has a smaller value than with phenylvinyl ethers¹³ which fact can be explained by the extension of the effect of the substituent across the whole molecule.

EXPERIMENTAL

Spectral Measurements

^1H -NMR spectra (chloroform-*d*, 25°C) were measured at 80 MHz with a Tesla BS 487C spectrometer using tetramethylsilane as the internal standard. Low-temperature measurements were run for solutions in acetone-*d*₆. ^{13}C -NMR spectra (chloroform-*d*) were measured at 25.04 MHz with a Jeol FX-100 spectrometer using tetramethylsilane as the internal standard.

Preparation of 5-nitro-2-vinylfuran and its ^1H -NMR data were described elsewhere¹⁶.

^{13}C -NMR data, δ : vinyl group $\text{—}\overset{\text{B}}{\text{C}}\text{H}=\overset{\text{A}}{\text{C}}\text{H}_2$ 120.0 (C_A), 123.5 (C_B); furan ring 155.3 (C_2), 110.3 (C_3), 113.4 (C_4), 151.9 (C_5).

(X-Phenyl)5-nitro-2-furylvinyl Ethers I—XII

A mixture of a substituted phenol (0.01 mol) and NaOH or KOH (0.01 mol) in water (20 ml) was added at room temperature to a stirred solution of 5-nitro-2-furylvinyltrimethylammonium bromide (a 4 : 1 mixture of *Z* and *E* isomers, *viz.*¹, 2.77 g, 0.01 mol). The colour of the mixture changes gradually from orange to dark brown, with concomitant evolution of trimethylamine. The mixture was concentrated at reduced pressure and the residue was purified by column chromatography on silica gel (100—250 mesh) using benzene and chloroform as the mobile phase. The *E* : *Z* = 1 : 1—3 : 1 ratio of isomers was determined by ^1H -NMR spectroscopy.

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