

^1H AND ^{13}C NMR STUDY OF SOME SUBSTITUTED 2-FURYL- AND 2-THIENYLETHYLENE DERIVATIVES

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The ^1H and ^{13}C NMR spectral data of 1-(5-nitro-2-furyl)-2-X-2-Y-ethylenes and some of their thienyl analogues are presented. Geometrical arrangement of the trisubstituted ethylenes was adduced from vicinal coupling constants $^3J(\text{C}, \text{H})$ for the carbon atom at the functional group attached to the double bond and the ethylene proton. The orientation of the heterocyclic ring towards the double bond of the side chain was determined from the ^1H NMR data. The preferred *s-cis* or *s-trans* conformations of 5-nitro-2-furylethylene derivatives is substituent at the double bond dependent; all thiophene derivatives under study were found in the *s-trans* conformation.

The ^1H NMR study of 2-furylethylene derivatives, 5-nitro-2-furyl- and 5-nitro-2-thienylethylene derivatives was reported in our preceding papers¹⁻⁶ and in those of other authors⁷⁻¹¹.

So far no systematic ^{13}C NMR study of 5-nitro-2-furylethylene derivatives has appeared; the ^1H and ^{13}C NMR investigation of 2-substituted 5-nitrofurans concerning also some 5-nitro-2-furylethylene derivatives was reported in¹². The extent of *p*- π conjugation in (X-phenyl)-5-nitro-2-furyl vinyl ethers was examined both by interpretation of their ^{13}C NMR spectra and by correlation of chemical shifts of carbon atoms and protons in ethylene with Hammett's σ constants⁴. Some 5-substituted 2-furyl- and 2-thienylethylene derivatives were published in¹³⁻¹⁶.

This paper concerns the interpretation of ^1H and ^{13}C NMR spectra of 1-(5-nitro-2-furyl)-2-X-2-Y-ethylenes I–XV and some of their 5-nitro-2-thienyl analogues XVI–XXII. Spectral parameters of some 2-furylethylene derivatives XXIII–XXVI are presented for comparison purpose. This paper is aimed to determine the arrangement of geometrical isomers of trisubstituted ethylenes related to furan and thiophene and to show the preferred conformation of the furan and thiophene rings in relation to the double bond employing the ^{13}C and ^1H NMR spectral data.

The ^{13}C chemical shifts and coupling constants are listed in Tables I and II. The respective signals were assigned to carbon atoms from the proton decoupled spectra

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on the basis of direct $^1J(\text{C}, \text{H})$ coupling constant values and the characteristic splitting due to long-range interactions. Signals appearing at the lowest magnetic field without a direct interaction with proton were ascribed to $\text{C}_{(5)}$ and $\text{C}_{(2)}$ of the heterocyclic ring. Signal of $\text{C}_{(5)}$ was seen as a broad multiplet as result of the quadrupole moment of nitrogen embodied in the nitro group. The $\text{C}_{(2)}$ signal of 5-nitro-2-furylethylenes was a triplet as a result of its interaction with H_3 and H_4 with coupling constant $J = 8.8 \text{ Hz}$; this signal occurred as doublet of a triplet for compounds *III*–*VI*, where also interaction with H_a took place the coupling constant

TABLE I
 ^{13}C NMR chemical shifts (δ , ppm) of compounds *I*–*XXVI*

Compound ^a	Isomer	2	3	4	5	α	β	γ	γ'	Ref. ^b
<i>I</i>	<i>E</i>	152.6	116.7	114.5	151.9	129.0	122.8	166.4	—	22
<i>II</i>	—	150.4	119.0	114.3	152.3	123.2	129.8	164.4	166.3	23
<i>III</i>	—	150.4	119.7	114.1	152.7	123.3	142.4	196.8	203.0	24
<i>IV</i>	—	149.6	120.7	114.0	152.5	125.5	126.7	162.6	164.4	24
<i>V</i> ^c	<i>E</i>	150.0	119.9	114.1	152.6	123.4	134.9	163.1	200.7	24
<i>VI</i> ^c	<i>Z</i>	150.0	120.7	114.1	152.6	125.3	134.5	195.1	165.7	24
<i>VII</i>	<i>E</i>	153.1	112.3	114.9	151.0	124.3	114.5	—	—	25
<i>VIII</i>	<i>Z</i>	152.4	114.5	114.1	150.5	120.7	113.8	—	—	25
<i>IX</i>	<i>Z</i>	150.9	118.8	114.0	151.8	126.4	118.0	163.1	—	26
<i>X</i>	—	151.4	114.7	114.1	150.5	124.8	95.5	—	—	26
<i>XI</i>	—	150.0	114.9	114.3	150.9	117.6	125.0	—	—	26
<i>XII</i>	<i>Z</i>	150.7	120.4	114.2	152.6	135.1	126.6	187.2	—	27
<i>XIII</i>	<i>E</i>	152.3	118.0	114.0	153.9	136.7	130.0	193.5	—	28
<i>XIV</i>	<i>E</i>	153.1	111.9	113.2	151.0	119.3	131.0	—	26.6	29
<i>XV</i>	<i>Z</i>	153.5	112.2	113.1	150.4	117.2	128.9	31.0	—	29
<i>XVI</i>	<i>E</i>	145.9	134.9	130.5	151.3	130.3	130.2	166.5	—	30
<i>XVII</i>	—	142.1	134.9	129.8	153.5	131.5	129.3	165.0	167.3	31
<i>XVIII</i>	<i>Z</i>	144.8	129.1	127.6	150.7	125.9	111.0	—	—	32
<i>XIX</i>	<i>Z</i>	143.5	135.3	129.2	152.2	133.3	117.5	163.3	—	30
<i>XX</i>	—	144.2	130.9	129.3	149.9	130.7	94.1	—	—	33
<i>XXI</i>	—	142.2	130.3	129.3	150.6	123.2	122.5	—	—	26
<i>XXII</i>	<i>Z</i>	142.4	134.6	129.5	153.1	129.5	124.9	162.9	—	34
<i>XXIII</i>	<i>E</i>	150.4	115.4	112.6	145.7	130.8	116.1	167.5	—	5
<i>XXIV</i>	<i>Z</i>	150.3	116.2	112.6	144.6	129.0	115.8	—	166.8	5
<i>XXV</i>	—	149.2	118.6	113.5	147.5	125.8	124.2	165.9	168.0	23
<i>XXVI</i>	—	152.2	115.1	112.3	144.4	125.9	124.9	168.6	14.1	6

^a Measured in hexadeuteriodimethyl sulfoxide, compounds *XIV*, *XV* and *XXV* in deuteriochloroform; ^b compounds were prepared according to the cited references; ^c a mixture of *E* and *Z* isomers.

$J(C_2, H_\alpha)$ being 4.8 Hz. The $C_{(2)}$ signal for 5-nitro-2-thienyl derivatives was a complex multiplet (interaction with H_α , H_3 and H_4).

TABLE II
Coupling constants $J(C, H)$ of compounds I—XXVI (in Hz)

Compound	C_γ, H_α	$C_{\gamma'}, H_\alpha$	C_3, H_3	C_4, H_4	C_α, H_α	C_β, H_α	Other constants ^a
I	5.8	—	183.6	188.5	167.0	6.8	167.0 (C_β, H_β), 3.9 (C_α, H_β)
II	7.8	10.7	184.6	188.5	165.0	3.9	—
III	7.7	10.7	184.6	188.5	165.0	^b	5.8 (CO, CH_3)
IV	7.8	10.7	184.6	188.5	166.0	^b	—
V	7.3	10.7	184.6	189.0	167.0	2.9	4.8 (C_2, H_α), 5.8 (CO, CH_3)
VI	7.7	11.7	182.6	187.5	163.1	2.9	4.8 (C_2, H_α)
VII	—	—	183.6	184.5	169.9	8.7	198.2 (C_β, H_β)
VIII	—	—	182.6	189.5	163.1	4.8	205.8 (C_β, H_β), 6.8 (C_α, H_β)
IX	4.9	—	184.6	188.5	162.1	^b	—
X	—	—	183.2	187.6	167.0	^b	—
XI	—	—	184.6	187.6	167.0	^b	—
XII	6.8	—	185.5	189.5	162.1	2.9	190.4 (C_γ, H_γ), 42.9 (C_β, H_γ)
XIII	8.8	—	184.6	189.1	161.2	^b	177.3 (C_γ, H_γ), 26.4 (C_β, H_γ)
XIV	—	6.8	183.6	186.5	165.0	^b	4.8 (C_α, CH_3)
XV	4.9	—	183.6	185.5	158.2	^b	5.8 (C_α, CH_3)
XVI	5.8	—	177.0	178.7	165.0	^b	166.5 (C_β, H_β)
XVII	7.8	10.7	175.8	179.7	165.0	3.9	3.5 (C_α, H_3)
XVIII	—	—	172.9	177.3	161.2	3.9	4.4 (C_α, H_3)
XIX	4.9	—	176.7	179.7	164.1	3.9	3.5 (C_α, H_3)
XX	—	—	175.8	178.7	166.0	^b	—
XXI	—	—	175.8	179.7	167.9	^b	3.9 (C_α, H_3)
XXII	4.9	—	177.2	181.8	165.2	3.9	—
XXIII	5.8	—	177.7	176.7	158.2	—	206.0 (C_5, H_5), 10.7 (C_5, H_4), 7.8 (C_5, H_3), 3.9 (C_4, H_3), 12.7 (C_4, H_5), 159.1 (C_β, H_β)
XXIV	—	13.6	178.7	176.7	158.2	4.8	204.1 (C_5, H_5), 10.7 (C_5, H_4), 7.8 (C_5, H_3), 3.9 (C_4, H_3), 12.7 (C_4, H_5), 166.0 (C_β, H_β)
XXV	7.8	10.7	176.7	177.7	161.1	4.8	208.0 (C_5, H_5), 10.7 (C_5, H_4), 7.8 (C_5, H_3), 3.9 (C_4, H_3), 12.7 (C_4, H_5)
XXVI	7.7	5.8	175.1	176.0	157.8	—	203.0 (C_5, H_5), 10.7 (C_5, H_4), 7.8 (C_5, H_3), 3.9 (C_4, H_3), 13.1 (C_4, H_5)

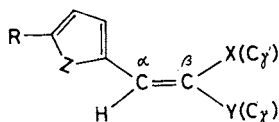
^a For compounds I—XV 8.8 (C_2, H_3 ; C_2, H_4), 2.9 (C_4, H_3), $J(C_3, H_4)$, (C_3, H_α) \leq 2.9; for XVI—XXII 4.8 (C_4, H_3), 3.9 (C_3, H_4), 12.7 (C_5, H_4); ^b unresolved.

Identification of signals belonging to $C_{(3)}$ and $C_{(4)}$ was based on the fact that the $C_{(3)}$ atom is more sensitive towards the effect of a substituent at the double bond than $C_{(4)}$. Assignment of these carbon atoms was proved by comparison of direct coupling constant $^1J(C, H)$ data with those of geminal $^2J(C, H)$ or vicinal $^3J(C, H)$ coupling constants. These values were contrasted with the reported data^{12,18}: $^1J(C_4, H_4) > ^1J(C_3, H_3)$; $^2J(C_4, H_3) > ^2J(C_3, H_4)$. Signal of $C_{(4)}$ was split by interaction with the H_3 proton, the coupling constant $^2J(C_4, H_3)$ value being 2.9 Hz. The $C_{(3)}$ signal was split due to an interaction with H_4 and the ethylene H_α into a doublet of triplet. The majority of furan derivatives have these coupling constant values low: $^2J(C_3, H_4)$, $^3J(C_3, H_\alpha) \leq 2.9$ Hz. Coupling constant values of thiophene derivatives $^2J(C_3, H_4)$, $^3J(C_3, H_\alpha) \sim 3.9$ Hz, $^2J(C_4, H_3) = 4.8$ Hz. Chemical shifts of $C_{(3)}$ carbon atoms of furan ring are also influenced by configuration on the double bond resulting from both the steric and anisotropic effects of substituents at $C_{(\beta)}$. This phenomenon has been observed^{5,6} with the corresponding isomers VII and VIII, V and VI, XXIII and XXIV, and with (X-phenyl)-5-nitro-2-furyl vinyl ethers⁴, where the $C_{(3)}$ signals of Z isomers were shifted downfield.

Values of direct coupling constants 1J of $C_{(\alpha)}$ with H_α for furan and thiophene derivatives are in the 161 – 167 Hz range. Long-range coupling constants with protons of the furan ring were not observed. The coupling constant of $C_{(\alpha)}$ with H_3 of the thiophene ring $^3J(C_\alpha, H_3)$ equaled 3.5 Hz. The $C_{(\beta)}$ atom of some compounds entered into interaction with H_α with coupling constant ~ 2.9 Hz, or alternatively, it appeared as a broad singlet. Assignment of carbon atoms was verified by a selective heteronuclear decoupling.

This paper was stimulated by the necessity to determine various geometrical isomers of furylethylene and thienylethylene derivatives. The insolubility of many derivatives in nonpolar solvents and the nonplanarity of the molecule made the unequivocal decision on the configuration at the double bond impossible when employing the 1H NMR and the additive increments method¹⁷. To ascribe the E or Z arrangement to the trisubstituted ethylenes, coupling constants $^3J(C, H)$ between $C_{(\gamma)}$ or $C_{(\gamma')}$ of substituents Y or X at $C_{(\beta)}$ at the double bond and the ethylene H_α were measured; $^3J(C, H)_{trans}$ is greater than $^3J(C, H)_{cis}$, what is an analogous criterion for E and Z isomers as is the $^3J(H, H)$ in 1H NMR spectrometry^{19,21}. This method makes it possible to determine the type of the majority of single isomers without concomitant measurement of their counterparts. The effect of substituents at the double bond on the magnitude of these constants was investigated with compounds I, XXI, XXIII and XXIV, the conformation of which could be unambiguously determined from vicinal coupling constants $^3J(H, H)$ of protons at the double bond. The coupling constants values $^3J(C, H)$ are in majority comparable with those reported for substituted phenylethylene derivatives²⁰. The coupling constant of E isomers of 3-(5-nitro-2-furyl)propenoic (I), 3-(5-nitro-2-thienyl)propenoic (XVI) and 3-(2-furyl)propenoic (XXIII) acids $^3J(COOH, H)_{cis} = 5.8$ Hz. The $^3J(CO, H)_{cis}$

coupling constant of compounds *II*–*VI*, *XVII*, having two carboxylic, ester or carbonyl groups at $C_{(\beta)}$ equaled 7.3–7.8 Hz, that of ${}^3J(\text{CO}, \text{H})_{\text{trans}}$ equaled 10.7 to 11.7 Hz. Electronegativity of the substituent influenced the coupling constant value ${}^3J(\text{CO}, \text{H})_{\text{cis}}$ towards lower values. This effect was observed when comparing compounds *IX* and *II* (4.9 and 7.8 Hz), *XIX* and *XVII* (4.9 and 7.8 Hz), *XII* and *XIII* (6.8 and 8.8 Hz).



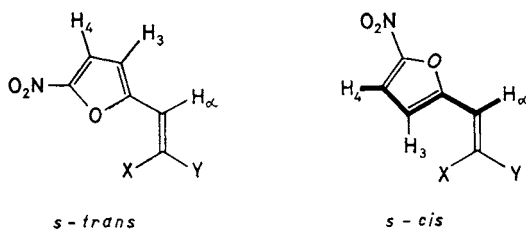
I – *XXII*, $\text{R} = \text{NO}_2$
XXIII – *XXVI*, $\text{R} = \text{H}$

	Z	X	Y		Z	X	Y
<i>I</i>	O	H	COOH	<i>XVI</i>	S	H	COOH
<i>II</i>	O	COOH	COOH	<i>XVII</i>	S	COOH	COOH
<i>III</i>	O	COCH ₃	COCH ₃	<i>XVIII</i>	S	Br	H
<i>IV</i>	O	COOC ₂ H ₅	COOC ₂ H ₅	<i>XIX</i>	S	Br	COOH
<i>V</i>	O	COCH ₃	COOC ₂ H ₅	<i>XX</i>	S	Br	Br
<i>VI</i>	O	COOC ₂ H ₅	COCH ₃	<i>XXI</i>	S	Cl	Cl
<i>VII</i>	O	H	Br	<i>XXII</i>	S	Cl	COOH
<i>VIII</i>	O	Br	H	<i>XXIII</i>	S	O	COOH
<i>IX</i>	O	Br	COOH	<i>XXIV</i>	O	COOH	H
<i>X</i>	O	Br	Br	<i>XXV</i>	O	COOH	COOH
<i>XI</i>	O	Cl	Cl	<i>XXVI</i>	O	CH ₃	COOCH ₃
<i>XII</i>	O	Br	CH=O				
<i>XIII</i>	O	H	CH=O				
<i>XIV</i>	O	CH ₃	Br				
<i>XV</i>	O	Br	CH ₃				

Configuration of compounds *XIV*, *XV* and *V*, *VI* could not be unambiguously determined by ${}^1\text{H}$ NMR spectrometry using the additive increment method¹⁷ for calculation of the chemical shift of olefinic proton since the difference of chemical shift of olefinic proton signals between the corresponding isomeric pairs ($\Delta\delta_{\text{exp}}(\text{Z} - \text{E})$ for *XIV* and *XV* in $\text{C}^2\text{HCl}_3 = 0.03$ ppm, $\Delta\delta_{\text{calc}} = 0.38$ ppm, $\Delta\delta_{\text{exp}}(\text{Z} - \text{E})$ for *V* and *VI* = 0.06, $\Delta\delta_{\text{calc}} = 0.38$ ppm) is very small. Arrangement of isomers could be unequivocally assigned by comparison of vicinal coupling constant values ${}^3J(\text{C}, \text{H})$. The reference substances for configuration determination of *V* and *VI* were compounds *III* and *IV*. Comparison with the analogously substituted phenylethylene derivatives showed²⁰ that the coupling constant values of carbonyl groups ${}^3J(\text{COCH}_3, \text{H})$ were found higher (*VI*: 7.7 against 6.6 Hz, *V*: 10.7 against 9.9 Hz) and for ethoxy-

carbonyl groups lower. Pure *V* and *VI* were measured in deuteriochloroform; in hexadeuteriodimethyl sulfoxide an immediate isomerization took place: from *V* and *VI* a mixture was formed with the *Z* to *E* ratio approximately 3 : 1, which was constant even after a longer standing of the solution. The effect of structure factors, as electronegativity of substituents at $C_{(\beta)}$ and steric interactions, were manifested with compounds *XIV*, *XV* and *XXVI* by the lowered value of ${}^3J(\text{CH}_3, \text{H})_{\text{trans}}$ coupling constant. Therefore, it could be problematic to ascribe the structure to one existing isomer. The structure of isomers *XIV* and *XV* was adduced from comparison of ${}^3J(\text{CH}_3, \text{H})$ coupling constant values ($E = 6.8$, $Z = 4.9$ Hz). The *E* isomer of compound *XXVI* was originally assigned this arrangement by ${}^1\text{H}$ NMR spectroscopy⁶, and later verified by following coupling constant values: ${}^3J(\text{CO}, \text{H})_{\text{cis}} = 7.7$ Hz and ${}^3J(\text{CH}_3, \text{H})_{\text{trans}} = 5.8$ Hz.

The ${}^1\text{H}$ NMR chemical shift and coupling constant values are listed in Table III. By analogy with our preceding papers⁴⁻⁶ the preferred conformation of furyl and thienyl substituents at the double bond was studied on the basis of coupling constant values ${}^5J(\text{H}, \text{H})$ between the olefinic H_α proton and the H_4 proton of the heterocyclic ring. The increased value of the coupling constant ${}^5J(\text{H}_4, \text{H}_\alpha) = 0.4-0.6$ Hz showed furan derivatives *VIII-XII*, *XV*, *XXIV* and *XXVI*, this being in favour of their preferred *s-cis* conformation. These protons revealed an enhanced interaction due to a five-valence *W*-shaped arrangement of H_4 and H_α in *s-cis* conformation of the furan ring with respect to the double bond.



Conformation of compounds *VIII*, *XXIV*, *XXXVI* as *s-cis* has already been established in deuteriochloroform in our papers^{5,6}. The same result followed from measurement in hexadeuteriodimethyl sulfoxide, too. 2-Bromo-1-(5-nitro-2-furyl)-1-propene was prepared as an *E* isomer *XIV* and *Z* isomer *XV*. The coupling constant values ${}^5J(\text{H}_4, \text{H}_\alpha)$ were obtained from spectra with decoupled methyl protons. The value of this constant has been found to be 0.5 Hz for the *s-cis* conformation of *Z* isomer and <0.2 Hz for *s-trans* conformation of *E* isomer. The difference in chemical shifts of H_3 between the isomers under study $\Delta\delta(Z - E) = 0.49$ ppm proved the assignment of the preferred *s-cis* and *s-trans* conformations for *Z* and *E* isomers, respectively. The H_3 signal for the *Z* isomer was downfield shifted due to a deshielding

TABLE III
 ^1H NMR data (in ppm on the δ scale, J in Hz) of compounds I—XXVI

Compound	Solvent	H ₃	H ₄	H α	H β	Other signals	J _{3,4}	J _{4,α}	J α,β
I	a	7.27	7.79	7.48	6.50		3.9	c	16.0
II	a	7.30	7.79	7.47	—		3.9	0.3	—
III	a	7.24	7.74	7.55	—	2.41 (CH ₃), 2.39 (CH ₃)	3.9	0.3	—
IV	a	7.34	7.75	7.63	—	4.38 (CH ₂), 1.28 (CH ₃)	3.9	0.3	—
V	a	7.29	7.78	7.49	—	2.48 (CH ₃), 4.26 (CH ₂), 1.27 (CH ₃)	3.9	c	—
V'	b	6.90	7.32	7.35	—	2.54 (CH ₃), 4.32 (CH ₂), 1.35 (CH ₃)	3.9	c	—
VI	a	7.31	7.77	7.70	—	2.43 (CH ₃), 4.37 (CH ₂), 1.29 (CH ₃)	3.9	c	—
VI	b	6.91	7.35	7.29	—	2.41 (CH ₃), 4.50 (CH ₂), 1.35 (CH ₃)	3.9	c	—
VII	a	6.93	7.69	7.48	7.29	—	3.9	c	14.4
VII	b	6.51	7.31	7.21	6.96	—	3.9	c	14.4
VIII	a	7.32	7.74	7.40	7.13	—	4.0	0.6	8.4
VIII	b	7.30	7.37	7.04	6.87	—	4.0	0.6	8.5
IX	a	7.62	7.79	8.13	—	—	4.0	0.5	—
X	a	7.22	7.72	7.93	—	—	4.0	0.6	—
X	b	7.23	7.30	7.44	—	—	4.0	0.6	—
XI	a	7.17	7.76	7.41	—	—	3.9	0.5	—
XI	b	7.00	7.37	6.85	—	—	3.9	0.5	—

TABLE III
(Continued)

Compound	Solvent	H ₃	H ₄	H _α	H _β	Other signals	J _{3,4}	J _{4,α}	J _{α,β}
XII	^a	7.77	7.81	8.47	—	9.43 (CH=O)	4.2	0.3	—
XIII ^d	^a	7.42	7.77	7.70	6.73	9.70 (CH=O)	3.9	^c	16.0
XIV ^b	^b	6.70	7.30	6.74	—	2.75 (CH ₃)	3.9	^c	—
XV ^b	^b	7.19	7.24	6.77	—	2.57 (CH ₃)	3.9	0.5	—
XVI ^a	^a	7.76	8.15	7.90	6.73	—	4.1	^c	16.0
XVII ^a	^a	7.64	8.11	7.80	—	—	4.3	^c	—
XVIII ^b	^b	7.16	7.86	7.31	6.57	—	4.3	^c	8.0
XIX ^a	^a	7.82	8.16	8.57	—	—	4.3	^c	—
XX ^b	^b	7.12	7.83	7.64	—	—	4.3	^c	—
XXI ^a	^a	7.43	8.08	7.67	—	—	4.3	^c	—
XXI ^b	^b	7.06	7.83	7.06	—	—	4.3	^c	—
XXII ^a	^a	7.79	8.16	8.32	—	—	4.3	^c	—
XXIII ^a	^a	6.93	6.61	7.40	6.17	7.80 (H ₅)	3.5	^c	16.0
XXIV ^a	^a	7.40	6.44	6.64	6.83	7.65 (H ₅)	3.5	0.6	12.6
XXV ^a	^a	7.03	6.67	7.40	—	—	3.5	0.2	—
XXVI ^b	^b	6.57	6.45	7.43	—	2.19 (CH ₃), 3.77 (OCH ₃)	3.5	0.5	—

^a Hexadeuteriodimethyl sulfoxide; ^b deuteriochloroform; ^c J_{4,α} < 0.2 Hz; ^d values in C²HCl₃ cf. ref.^{1,2}.

effect of the bromine in an *s-cis* conformation; the same behaviour was observed when comparing spectra of *VII* and *VIII* and the corresponding isomers of other furylethylene derivatives^{5,6}.

All thiophene derivatives *XVI*–*XXII* exist in the preferred *s-trans* conformation. No interactions between H_4 and H_α atoms were seen in the 1H NMR spectra. Differences in conformations of the furan (*s-cis*) and thiophene (*s-trans*) rings with respect to the double bond could be observed when comparing coupling constants $^5J(H_4, H_\alpha)$ of analogous furan and thiophene derivatives *VIII* and *XVIII*, *X* and *XX*, *XI* and *XXI*, *IX* and *XIX* (Table III). Like differences were also reported with other furyl- and thienylethylene derivatives^{6–9}. Orientation of the thiophene ring was not influenced by the substituent at the double bond or by configuration of the double bond in contrast to that of the furan skeleton.

EXPERIMENTAL

The ^{13}C NMR spectra were measured with a Jeol FX-100 apparatus in 10 mm cells at 25.05 MHz, at a 6 000 Hz spectral width, 8 K data points, 45° flip angle and 21°C sample temperature. The chemical shifts were determined with a ± 0.06 ppm and coupling constants with a ± 0.74 Hz accuracies, respectively. The 1H NMR spectra were recorded with a Tesla BS 487 C spectrometer operating at 80 MHz at 25°C with tetramethylsilane as an internal standard. The chemical shift values were read with a ± 0.01 ppm, the coupling constants with a ± 0.05 Hz accuracies, respectively. Signals were ascribed by means of the INDOR technique, the long-range interactions were evidenced by a decoupling experiment. The spectra were taken with hexadeuteriodimethyl sulfoxide and deuteriochloroform solutions.

Preparation of compounds *I*–*XXVI* has already been published, or will be published. Citations are presented in Table I at the proper place.

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