

SYNTHESIS AND SPECTRAL PROPERTIES OF TRISUBSTITUTED ETHYLENES OF THE 5-NITROFURAN SERIES

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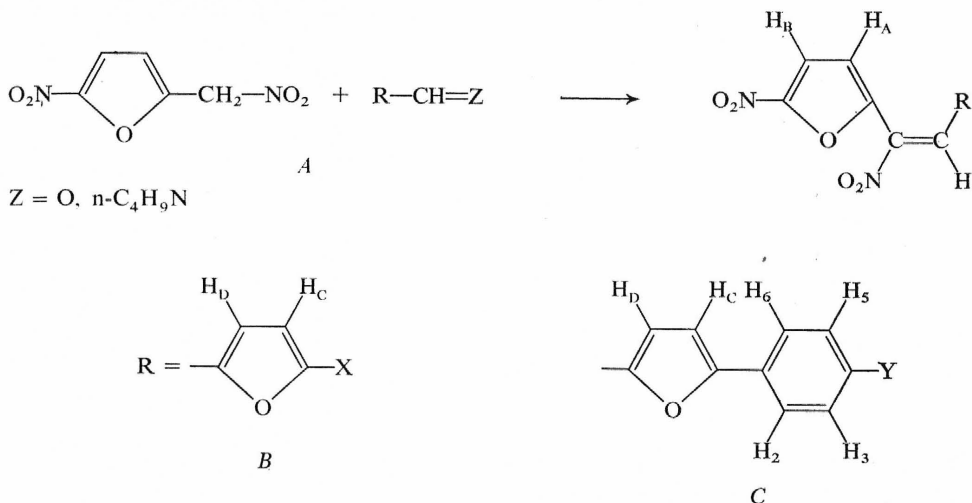
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Condensation of 5-nitro-2-furylnitromethane (*A*) with furancarbaldehydes or phenylfurancarbaldehydes, catalysed by ammonium acetate in a mixture of acetic acid and benzene, afforded 1-(5-nitro-2-furyl)-1-nitro-2-(5-*X*-furyl)ethylenes (*B*), where *X* is H, CH₃, Br, I or NO₂, or 1-(5-nitro-2-furyl)-1-nitro-2-[5-(*Y*-phenyl)-2-furyl]ethylenes (*C*), wherein *Y* is H, 4-CH₃, 4-COOCH₃, 4-NO₂, 4-Cl, 4-Br or 2-Cl. The same products were obtained by reaction of the compound *A* with azomethines of the corresponding aldehydes in acetic acid. The IR, UV and ¹H-NMR spectra of the synthesized compounds are interpreted and configuration of their double bond is determined on the basis of additive increments.

In our previous paper¹ we published the synthesis of trisubstituted ethylenes which were prepared by condensation of 5-nitro-2-furylnitromethane (*A*) with aromatic aldehydes. The present communication describes the preparation of 1-(5-nitro-2-furyl)-1-nitro-2-(5-*X*-2-furyl)ethylenes (*B*) and 1-(5-nitro-2-furyl)-1-nitro-2-[5-(*Y*-phenyl)-2-furyl]ethylenes (*C*) consisting in condensation of the compound *A* with furancarbaldehydes, phenylfurancarbaldehydes or azomethines of these aldehydes (Scheme 1). The yields range from 30% to 90% (Table I). For compounds *I*, *II*, *V*, *VI* and *X*, procedure 3 is the method of choice, whereas for the preparation of the other compounds procedure 2 is the best.

The UV spectra of most of the compounds *B* and *C* display two absorption bands in the regions 345–295 nm and 440–357 nm. The first band can be attributed to electronic transitions in the furan² or benzene³ rings. The second band (K-band), corresponding to electronic transitions of the whole conjugated system, affords important information about molecular planarity of the synthesized compounds. Fig. 1 depicts the absorption curves of planar compounds (curves *a* and *b*)^{4,5} together with typical curves of some synthesized compounds (curves *c*, *d*). The planar systems *a* and *b* show strong K-bands in the visible spectral region whereas in the spectra of the trisubstituted ethylenes (*c* and *d*) this band is hypsochromically shifted for

15–20 nm. These UV data are in accord with the molecular models and prove that molecules of this type are non-planar.



SCHEME 1

The structure of the compounds *I–XIII* is confirmed by their IR and ¹H-NMR spectra (Table II and III). The IR spectra of compounds *B* exhibit a medium absorption band due to $\nu(\text{C}=\text{C})$ in the region 1655–1640 cm⁻¹, compounds *C* absorb at 1662–1650 cm⁻¹. The effect of substituents on the position of these bands is insignificant. All the compounds *B* and *C* display two $\nu_s(\text{NO}_2)$ bands in the regions 1340–1315 cm⁻¹ and 1365–1355 cm⁻¹; one is due to NO₂ group bonded to the ethylenic α -carbon (relative to the 5-nitrofuran moiety), the second corresponds

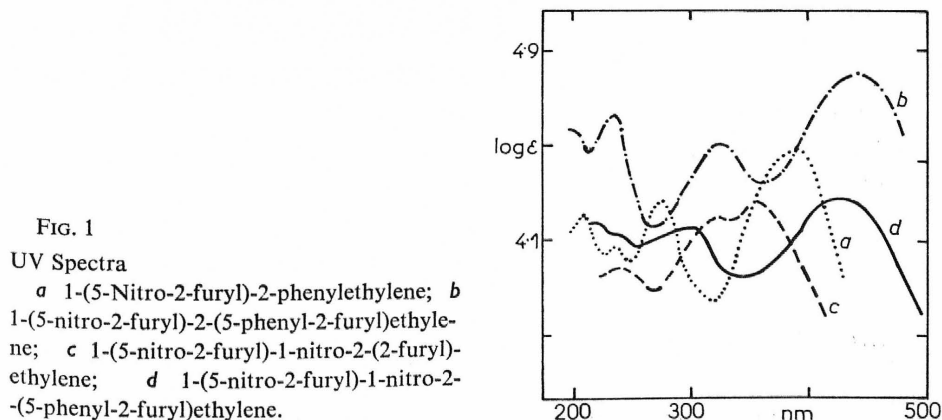


FIG. 1
UV Spectra
a 1-(5-Nitro-2-furyl)-2-phenylethylene; *b* 1-(5-nitro-2-furyl)-2-(5-phenyl-2-furyl)ethylene; *c* 1-(5-nitro-2-furyl)-1-nitro-2-(2-furyl)ethylene; *d* 1-(5-nitro-2-furyl)-1-nitro-2-(5-phenyl-2-furyl)ethylene.

to the NO₂ group attached to the furan ring. The compound X exhibits three bands due to three NO₂ groups in its molecule. Bands, corresponding to $\nu_{as}(\text{NO}_2)$, occur in the region 1560–1540 cm⁻¹ as a single absorption band of medium intensity: showing thus that this type of bands due to NO₂ groups bonded to the furan ring and to the ethylenic α -carbon overlap each other.

TABLE I
Synthesized Compounds

Compound X, Y	M.p., °C (yield, %)	Formula (m.w.)	Calculated/Found			Procedure
			% C	% H	% N	
1-(5-Nitro-2-furyl)-1-nitro-2-(5-X-2-furyl)ethylenes (B)						
<i>I</i>	116–117	C ₁₀ H ₆ N ₂ O ₆	48·00	2·41	11·20	1, 3
H	(28·0)	(250·2)	47·60	2·31	11·07	
<i>II</i>	140–142	C ₁₁ H ₈ N ₂ O ₆	50·00	3·05	10·60	1, 3
CH ₃	(36·0)	(264·2)	50·33	3·25	10·65	
<i>III</i>	202–203	C ₁₀ H ₅ BrN ₂ O ₆	36·49	1·53	8·51	2, 3
Br	(67·0)	(329·1)	36·13	1·46	8·22	
<i>IV</i>	208–211 ^a	C ₁₀ H ₅ IN ₂ O ₆	32·20	1·34	7·45	2, 3
I	(71·5)	(376·1)	32·22	1·37	7·49	
<i>V</i> (E)	134–137	C ₁₀ H ₅ N ₃ O ₈	40·69	1·71	14·32	3, 2
NO ₂	(17·2)	(295·2)	40·50	1·80	14·22	
<i>VI</i> (Z)	175–178	C ₁₀ H ₅ N ₃ O ₈	40·69	1·71	14·32	3, 2
NO ₂	(30·5)	(295·2)	40·48	1·68	14·20	
1-(5-Nitro-2-furyl)-1-nitro-2-[5-(Y-phenyl)-2-furyl]ethylenes (C)						
<i>VII</i>	136–139	C ₁₆ H ₁₀ N ₂ O ₆	58·89	3·09	8·58	2, 1
H	(66·0)	(326·3)	58·46	3·06	8·14	
<i>VIII</i>	165–168	C ₁₇ H ₁₂ N ₂ O ₆	59·99	3·55	8·23	2, 3
4-CH ₃	(35·6)	(340·3)	59·70	5·50	8·20	
<i>IX</i>	185–187	C ₁₈ H ₁₂ N ₂ O ₈	56·25	3·15	7·29	2, 3
4-COOCH ₃	(83·2)	(384·3)	55·90	3·00	6·99	
<i>X</i>	114–116	C ₁₆ H ₉ N ₃ O ₈	51·75	2·44	11·32	2, 3
4-NO ₂	(41·2)	(371·2)	51·55	2·32	11·12	
<i>XI</i>	172–173	C ₁₆ H ₉ ClN ₂ O ₆	53·27	2·52	7·77	2, 3
4-Cl	(91·5)	(360·7)	53·29	2·57	7·73	
<i>XII</i>	162–165	C ₁₆ H ₉ BrN ₂ O ₆	49·49	2·34	7·20	2, 3
4-Br	(70·5)	(389·2)	49·25	2·31	7·01	
<i>XIII</i>	123–125	C ₁₆ H ₉ ClN ₂ O ₆	53·27	2·52	7·77	2, 3
2-Cl	(71·0)	(360·7)	53·24	2·61	7·72	

^a Decomposition.

As seen from the $^1\text{H-NMR}$ spectra (Table III) the substituent X in the position 5 of the furan (or Y-phenylfuran) ring does not practically affect the position of the ethylenic proton signal. This fact is in accord with the mentioned non-planarity of these systems. $^1\text{H-NMR}$ spectra confirm that the condensation of compound A with furan- or phenylfurancarbaldehydes leads to single geometric isomers whose (E)-configuration was determined on the basis of additive increments^{6,7} (for 5-nitro-

TABLE II
UV (nm) and IR (cm^{-1}) Spectra of Compounds I–XIII

Compound	$\lambda_{\text{max}}/(\log \epsilon)$		$\nu_s(\text{COC})$	$\nu_s(\text{NO}_2)$	$\nu_{\text{as}}(\text{NO}_2)$	$\nu(\text{C}=\text{C})$
<i>I</i>	314 (4·19)	357 (4·24)	1 030	1 320 1 358	1 555	1 655
<i>II</i>	317 (4·13)	381 (4·20)	1 030	1 315 1 360	1 545	1 655
<i>III</i>	302 (4·01)	420 (4·32)	1 035	1 340 1 355	1 560	1 640
<i>IV</i>	308 (4·03)	425 (4·35)	1 035	1 335 1 355	1 560	1 640
<i>V</i>	310 (4·31)	372 (4·15)	1 035	1 320 1 355 sh	1 555	1 640
<i>VI</i>	310 (4·23)	392 (4·18)	1 030	1 325 1 355	1 555	1 640
<i>VII</i>	295 (4·16)	427 (4·29)	1 040 sh	1 320 1 357	15 550	1 650
<i>VIII</i>	300 (4·20)	440 (4·30)	1 028 1 040	1 320 1 357	1 542	1 650
<i>IX</i>	307 (4·04)	428 (4·15)	1 020 1 040	1 320 1 355	1 540	1 650
<i>X</i>	345 (4·60)	431 (4·11)	1 020 1 040	1 325 1 340 1 355	1 550	1 660
<i>XI</i>	300 (4·20)	435 (4·34)	1 020 1 040	1 320 1 355	1 540	1 650
<i>XII</i>	295 (4·23)	440 (4·38)	1 015 1 040	1 320 1 365	1 545	1562
<i>XIII</i>	295 (4·19)	411 (4·35)	1 020 1 040	1 320 1 355	1 550	1 662

furan ring we used the increment corresponding to an aryl group). This result was confirmed by measuring the spectra not only of the pure compounds but also of the crude reaction products. Condensation of the compound *A* with 5-nitro-2-furan-carbaldehyde affords a mixture of (*E*)- and (*Z*)-isomers in the ratio 1 : 2. For both the isomeric compounds *V* (*E*-isomer) and *VI* (*Z*-isomer) the chemical shifts of the ethylenic protons are in good accord with the calculated values (*E*: 8.23 ppm; *Z*: 7.45 ppm). The pure isomers *V* and *VI* were obtained by fractional crystallisation from benzene. They display different IR and UV spectra (Table II), the latter resembling those of *cis*- and *trans*- α -nitrostilbenes⁸. The hypsochromic shift (20 nm) of the K-band in the UV spectrum of the (*E*)-isomer *V* relative to the (*Z*)-isomer *VI*, as well as the hyperchromic shift (*V*: log ϵ 4.15; *VI*: log ϵ 4.18) indicate that the steric congestion of substituents at the ethylenic double bond is larger in the isomer *V* than in *VI* and, consequently, in the former compound the system deviates more from planarity.

TABLE III
¹H-NMR Spectra of Compounds *I*–*XIII*
(δ , ppm; *J*, Hz)

Compound	—CH=	H _A ^a	H _B ^a	<i>J</i> _{AB}	H _C ^a	H _D ^a	<i>J</i> _{CD}	H ₂₆ ^b	H ₃₅ ^b
<i>I</i>	8.53	7.27	7.87	3.8	6.78	7.47	3.6	—	—
<i>II</i>	8.44	7.25	7.87	3.8	6.49	7.42	3.6	—	—
<i>III</i>	8.46	7.30	7.91	3.8	6.95	7.47	3.6	—	—
<i>IV</i>	8.44	7.25	7.90	3.9	7.00	7.32	3.6	—	—
<i>V</i>	8.58	7.36	7.91	3.9	7.75	7.58	3.8	—	—
<i>V</i> ^c	8.14	7.14	7.47	3.8	7.34 s	—	—	—	—
<i>VI</i> ^c	7.31	6.95	7.40	3.8	7.28	7.21	—	—	—
<i>VII</i>	8.54	7.38	8.01	3.8	7.33	7.63	3.9	(7.12—7.62) ^d	
<i>VIII</i>	8.52	7.36	8.01	3.9	7.26	7.62	3.8	7.33	7.20
<i>IX</i>	8.56	7.40	8.06	3.8	7.47	7.63	3.8	7.56	7.94
<i>X</i>	8.56	7.42	8.05	3.9	7.58	7.63	3.9	7.67	8.23
<i>XI</i>	8.53	7.39	7.99	3.8	7.36	7.62	3.8	7.46 s	
<i>XII</i>	8.53	7.39	7.99	3.9	7.35	7.61	3.8	7.37	7.60
<i>XIII</i>	8.60	7.36	7.96	3.8	7.40	7.65	3.8	(7.23—7.80) ^d	

^a Doublet; ^b $J_{23} = J_{56} = 9$ Hz; ^c measured in CDCl₃; ^d multiplet of aromatic protons.

EXPERIMENTAL

Yields, melting points and analytical data for the synthesized compounds are given in Table I. IR spectra were taken on a UR-20 (Zeiss, Jena) spectrophotometer in the region $700-3600\text{ cm}^{-1}$ in saturated chloroform solutions (0.4 or 0.6 mm cells). The instrument was calibrated using a polystyrene foil; accuracy $\pm 1\text{ cm}^{-1}$. Electronic absorption spectra were measured in the region 200–800 nm on a Specord UV VIS (Zeiss, Jena) instrument in dioxane (1 cm cells, concentration $5 \cdot 10^{-5}\text{ mol l}^{-1}$) and the data are listed in Table II. $^1\text{H-NMR}$ spectra were measured on an 80 MHz instrument BS-487C (Tesla, Brno) in hexadeuteriodimethyl sulfoxide using tetramethylsilane as internal standard (δ scale); the data are given in Table III.

Procedure 1 (compounds *I* and *II*): The corresponding aldehyde (0.01 mol) and ammonium acetate (0.1 g) were added to a solution of the compound *A* (1.72 g; 0.01 mol) in conc. acetic acid. The mixture was stirred at room temperature for 8–12 h, poured into ice-water (about 100 ml), the separated compound collected on filter and crystallized from acetic acid.

Procedure 2 (compounds *III*, *IV*, *VII–XII*): Azomethine (0.01 mol), prepared from the appropriate aldehyde and butylamine⁹, was added to a solution of the compound *A* (0.01 mol) in conc. acetic acid at room temperature. The mixture soon began to deposit crystals which after 24 h were filtered and crystallized from acetic acid.

Procedure 3 (compounds *I*, *II*, *V*, *VI* and *X*): A solution of the compound *A* (1.72 g; 0.01 mol) in benzene was mixed with the corresponding aldehyde (0.01 mol), acetic acid (5 ml) and ammonium acetate (0.1 g) and the formed water was removed by azeotropic distillation during 8–10 h. The mixture was poured into water (about 100 ml), the benzene layer separated, washed twice with 5% sodium hydrogen carbonate solution, dried over sodium sulfate and the solvent distilled off. The product was crystallized from benzene.

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