SPATIAL ARRANGEMENT
# OF 1-(2-FURYL)-2-METHOXYCARBONYL-4-(5-X-2-FURYL)-
BUTADIENES

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The ^{1}H NMR spectrometry of 1-(2-furyl)-2-methoxycarbonyl-4-(5-X-2-furyl)butadienes showed the double bonds of the butadiene backbone to have *E, E*, or *E, Z* configurations and *s-trans* conformation. The unsubstituted furan ring is in an *s-cis* conformation with respect to the double bond of the butadiene chain. The *E, E* isomers and the *E, Z* isomers have the substituted furan ring out of the butadiene backbone plane.

The spatial arrangement of furylethylene derivatives by ^{1}H NMR spectrometry has been reported in our preceding papers[1-5] and also by other authors[6-10]. This paper concerns the spatial arrangement of 1-(2-furyl)-2-methoxycarbonyl-4-(5-X-2--furyl)butadiene derivatives. Compounds having the *E, E*, or *E, Z* configurations at double bonds of the butadiene chain can exist as various conformers, and also
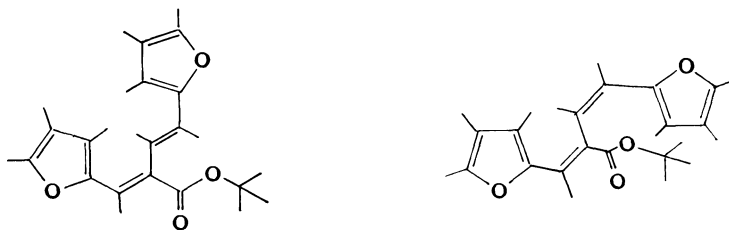
E, E   *E, Z*
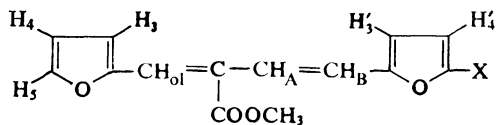
II, X = CH$_3$	V, X = I
III, X = H	VI, X = COOCH$_3$
IV, X = Br	VII, X = NO$_2$

the double bonds can have various conformations with respect to furan rings. Investigation of spectral data made it possible to ascertain their relation to geometry of compounds under study. To determine the prevalent conformations, the stereospecific long-range coupling constants $^5J_{H,H}$ between olefinic protons of the butadiene backbone and H_{ol} and H_4 of the unsubstituted furan ring[9,10] were employed. The structure was further evidenced by NOE-experiment and measurement using a shift reagent.

1-(2-Furyl)-2-methoxycarbonyl-4-(5-X-2-furyl)-butadienes $II-VII$ were prepared from 5-X-2-furaldehydes and 2-methoxycarbonyl-3-(2-furyl)-2-propenyltriphenylphosphonium bromide (I). The latter was synthesized from methyl 2-bromomethyl--3-(2-furyl) propenoate[11] and triphenylphosphine in benzene. The corresponding ylide was generated from I with sodium methoxide in methanol. The isomeric products coming from the Wittig reaction were separated by column chromatography on silica gel.

TABLE I

^{1}H NMR Data (δ, ppm, J, Hz) of 1-(2-furyl)-2-methoxycarbonyl-4-(5-X-2-furyl)butadienes

Compound X	Isomer	H_{ol}	H_A	H_B	J_{AB}	H_3	H_4	H_5	$H_{3'}$	$H_{4'}$	OCH_3	Other
II	Z	7·39	6·42	6·27	12·5	6·66	6·40	7·45	6·18	6·89	3·61	2·20
CH_3	E	7·20	7·45	7·20	16·0	6·67	6·48	7·57	6·26	6·00	3·81	2·33
III	Z	7·46	6·36	6·49	12·5	6·68	6·42	7·47	6·28		3·69	7·31
H	E	7·23	7·58	7·28	16·0	6·67	6·47	7·57	6·37		3·89	7·41
IV	Z	7·44	6·39		—	6·67	6·43	7·49	6·23		3·68	—
Br	E	7·25	7·49	7·16	16·0	6·68	6·50	7·60	6·31		3·82	—
V	Z	7·44	6·38		—	6·67	6·43	7·48	6·17	6·45	3·68	—
I	E	7·25	7·53	7·20	16·0	6·69	6·52	7·61	6·26	6·56	3·82	—
VI	Z	7·52	6·58		—	6·72	6·46	7·53	6·35	7·10	3·61	3·86
$COOCH_3$	E	7·26	7·77	7·33	16·0	6·72	6·51	7·64	6·46	7·10	3·81	3·88
VII	Z	7·57	6·56	6·77	12·4	6·74	6·47	7·53	6·46	7·24	3·72	—
NO_2	E	7·40	7·99	7·47	16·0	6·78	6·56	7·69	6·54	7·33	3·85	—

$J_{H,H}$ (Hz)

II	Z	$H_4H_{ol} = 0·5$; $H_{ol}H_B = 1·4$		E	$H_4H_{ol} = 0·5$; $H_{ol}H_A = 1$
III	Z	$H_4H_{ol} = 0·4$		E	$H_4H_{ol} = 0·5$; $H_{ol}H_A = 1$
IV	Z	$H_4H_{ol} = 0·5$		E	$H_4H_{ol} = 1·0$
V	Z	$H_4H_{ol} = 0·5$; $H_BH_{ol} = 1·4$		E	$H_4H_{ol} = 0·5$
VI	—			E	$H_AH_{ol} = 1·0$
VII	Z	$H_4H_{ol} = 0·5$; $H_BH_{ol} = 1·5$		E	$H_4H_{ol} = 0·5$; $H_BH_{ol} = 1·1$

The respective isomers at the newly formed double bond were distinguished considering the magnitude of the vicinal coupling constant of protons H_A and H_B. Its magnitude is greater for the E isomers (16 Hz) than for the Z isomers (12·5 Hz, cf. Table I). The E configuration of the double bond to which methoxycarbonyl group and the unsubstituted furan ring are attached is the same as with methyl 2-methyl-3-(2-furyl)-propenoate[5].

The E, Z isomers are characteristic of a stereospecific long-range coupling constant $^5J_{H_{o1},H_B}$. Its value, ranging from 1·4 to 1·5 Hz indicates the arrangement of five bonds to be W-shaped[12]. This is in favour of the preferred s-trans conformation of the butadiene skeleton of E, Z isomers, what is in line with the fact that the gradient of the induced chemical shift for proton H_A is greater than that for H_B. Consequently, the distance of H_A from the coordination site of the shift reagent (oxygen of the methoxycarbonyl[13]) is shorter than that of H_B. Dreiding models showed that the distance H_A—O $\simeq$ 0·45 nm and H_B—O $\simeq$ 0·52 nm. The s-trans conformation of the butadiene chain of E, Z isomers is also backed by a higher value of the gradient induced shift $H_{5'}$, when compared with H_5; this phenomenon is due to a shorter distance of $H_{5'}$ from the carbonyl oxygen of the methoxycarbonyl group (Table II). The preferred conformation of furan rings was determined by analogy to that of the butadiene chain employing the long-range coupling constant between H_{o1} and H_4 and between H_B and $H_{4'}$. Since the coupling constant $^5J_{H_{o1},H_4}$ was observed, the unsubstituted furan ring might be in a prevailing s-cis conformation to double bond[5,8] and the substituted furan ring is probably not in the butadiene chain plane. The preferred conformations of E, E isomers of compounds $II - VII$ were adduced

TABLE II
Gradient values of the induced chemical shift (δ, ppm) of 1,4-bis(2-furyl)-2-methoxycarbonyl-butadiene

Parameter	H_{o1}	H_A	H_B	H_5	$H_{5'}$
		E, Z Isomer			
K^a	11·26	4·96	3·84	0·21	1·96
r^b	0·999	0·999	0·999	0·999	0·999
		E, E Isomer			
K^a	10·05	7·69	3·90	0·38	0·60
r^b	0·999	0·999	0·990	0·980	0·990

^{a} Slope of the induced chemical shift; ^{b} correlation coefficient.

analogously as for E, Z-isomers from long-range coupling constants, using a shift reagent, and from NOE-experiment.

After irradiation of proton H_3 in the NOE-experiment a 10% raise of the proton H_A intensity occurs. This result indicates that double bonds of the butadiene chain are in a predominant s-*trans* conformation and the unsubstituted furan ring in a prevailing s-*cis* conformation. The s-*trans* conformation of double bonds is also indicated by the magnitude of the coupling constant $^4J_{H_{01},H_A} = 1.0-1.1$ Hz (ref.[12]) and a greater gradient of the induced chemical shift of proton H_B than H_A (distance H_B—O $\simeq$ 0.37 nm, H_A—O $\simeq$ 0.45 nm), and by a virtually equal gradient of the induced chemical shift of H_5 and $H_{5'}$ following from almost the same distance of these protons from the coordination site of the shift reagent (Table II). The magnitude of the stereospecific long-range coupling constant $^5J_{H_{01},H_4} = 0.5$ Hz is in favour of the s-*cis* conformation, too. A similar coupling constant between protons H_B and $H_{4'}$ was not proved. The IR spectra of these substances reveal bands of carbonyl stretching vibrations of the methoxycarbonyl group at $1\,706-1\,715$ cm^{-1} as the most intense. Two bands of medium intensity at $1\,556-1\,599$ and $1\,594-1\,618$ cm^{-1} were ascribed to stretching vibrations of conjugated double bonds. The E, E isomers show a characteristic band of an out-of-plane bending vibration of C—H bond of *trans* isomers at $963-966$ cm^{-1} (Table III).

A linear relationship between the Hammet σ constants of substituents X at furan ring and the chemical shift value of the olefinic proton were found (Table IV). The transmission coefficient for E, E isomers is greater than for E, Z isomers. The λ_{max} of the most long-wave band corresponding to $\pi^* \leftarrow \pi$ electronic transition of the whole conjugated system for E, E isomers is at $363-422$ nm, whilst for E, Z isomers at $330-374$ nm.

Considering the spectral data of 1-(2-furyl)-2-methoxycarbonyl-4-(5-X-2-furyl)-butadienes $(II-VII)$ one is entitled to assume the geometric structure of these substances to approach that shown in Scheme 1; the substituted furan ring of E, Z isomers is twisted out of the plane formed by the butadiene backbone and the unsubstituted furan ring.

EXPERIMENTAL

The IR spectra of chloroform solutions were measured with a UR-20 (Zeiss, Jena) spectrophotometer in 0.26 nm-cells at a 10^{-2} mol l^{-1} concentration. The UV spectra were recorded with a UV-VIS (Zeiss, Jena) apparatus in 10 mm-cells at a $5 . 10^{-5}$ mol l^{-1} concentration, the ^{1}H NMR spectra were run with a Tesla BS 487 C spectrometer operating at 80MHz in deuterio-chloroform containing tetramethylsilane as reference. Signals were assigned by means of the INDOR technique, the long-range coupling constants were verified by decoupling experiments. The shift reagent used was tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-3,5-octanedionato)europium.

TABLE III

IR (cm^{-1}) and UV $(nm, m^2\,mol^{-1})$ spectra of 1-furyl-2-methoxycarbonyl-4-(5-X-2-furyl-butadienes

Compound X	Isomer	ν(C=C)	ν(C=C)	ν(C=O)	ν(C—O)	γ(C—H)	λ_{max} (log ε)
II CH$_3$	Z	1 605	1 586	1 706	1 278	—	200 (4·42) 280 (4·20) 346 (4·21)
	E	1 619	1 599	1 708	1 293	964	202 (4·00) 283 (4·17) 372 (4·32)
III H	Z	1 607		1 708	1 279	—	200 (4·41) 273 (4·11) 330 (4·30)
	E	1 618	1 598	1 712	1 287	964	200 (4·43) 278 (4·39) 363 (4·42)
IV Br	Z	1 606		1 711	1 270	—	200 (4·42) 280 (4·32) 337 (4·38)
	E	1 618	1 599	1 710	1 285	964	204 (4·14) 280 (4·23) 370 (4·43)
V I	Z	1 597		1 706	1 270	—	207 (4·07) 294 (4·13) 348 (4·23)
	E	1 612	1 593	1 708	1 276	965	207 (4·05) 297 (4·21) 381 (4·35)
VI COOCH$_3$	Z	1 600	1 571	1 715	1 294	—	207 (4·12) 295 (4·00) 357 (4·00)
	E	1 594	1 570	1 715	1 302	963	207 (4·10) 297 (4·18) 379 (4·28)
VII NO$_2$	Z	1 611	1 566	1 708	1 251	—	207 (4·10) 324 (4·35) 374 (4·21)
	E	1 597	1 567	1 709	1 285	966	200 (4·61) 326 (4·41) 422 (4·31)

TABLE IV

Dependence of H_{01} chemical shift upon σ constants of substituents X

Isomer	n	ϱ^a	r^b	Standard deviation
E, E	6	0·20	0·94	0·027
E, Z	6	0·18	0·90	0·030

[a] Transmission coefficient of the substituent; [b] correlation coefficient.

TABLE V

1-(2-Furyl)-2-methoxycarbonyl-4-(5-X-2-furyl)butadienes

Compound X	Yield, %[a]	Formula (M_r)	Isomer	Calculated/Found % C	% H
II CH$_3$	80	C$_{15}$H$_{14}$O$_4$ (258·3)		69·75	4·29
			Z	69·70	4·20
			E	69·58	4·18
III H	85	C$_{14}$H$_{12}$O$_4$ (244·2)		68·84	4·95
			Z	68·52	4·70
			E	68·70	4·75
IV Br	80	C$_{14}$H$_{11}$BrO$_4^{b}$ (323·1)		52·03	3·43
			Z	51·90	3·25
			E	52·10	3·32
V I	85	C$_{14}$H$_{11}$IO$_4^{c}$ (370·1)		45·43	2·99
			Z	44·10	2·90
			E	44·05	2·86
VI COOCH$_3$	85	C$_{16}$H$_{14}$O$_6$ (302·3)		63·57	4·66
			Z	62·59	4·50
			E	62·80	4·60
VII NO$_2$	88	C$_{14}$H$_{11}$NO$_6^{d}$ (289·2)		58·13	3·83
			Z	58·22	3·70
			E	58·05	3·85

[a] Oily product, m.p. of (Z)-*VII* 104—106°C, m.p. of (E)-*VII* 128—129°C; [b] calculated: 24·72% Br; found 24·55% Br for Z, 24·50% for E; [c] calculated: 34·29% I; found: 34·11% I for Z, 32·30% I for E; [d] calculated: 4·84% N, found: 4·80% N for Z, 4·74% N for E.

2-Methoxycarbonyl-3-(2-furyl)-2-propenyltriphenylphosphonium Bromide (*I*)

Triphenylphosphine (16·2 g, 0·1 mol) and methyl 2-bromomethyl-3-(2-furyl)propenoate (24·5 g, 0·1 mol) were refluxed in benzene for 30 min. The product, which separated during the reaction, was filtered off and thoroughly washed with benzene. The dried product, (90%-yield) sufficiently pure for further experiment, had m.p. 177°C. For $C_{27}H_{24}BrO_3O$ (507·4) calculated: 63·90% C, 4·76% H, 15·75% Br; found: 63·81% C, 4·69% H, 15·70% Br.

1-(2-Furyl)-2-methoxycarbonyl-4-(5-X-2-furyl)butadienes *II— VII*

A mixture consisting of *I* (50 mmol) and 5-X-2-furaldehyde (50 mmol) in methanol (50 ml) was added to sodium methoxide (50 mmol) in methanol (100 ml). After a 5h-reflux water (100 ml) was added and the separated oily product was dissolved in benzene, dried, concentrated and chromatographed on a silica gel column with benzene as eluent. Yield of the respective products refers to the mixture of isomers (Table V).

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