

## TRISUBSTITUTED ETHYLENES OF THE 5-NITROFURAN SERIES\*

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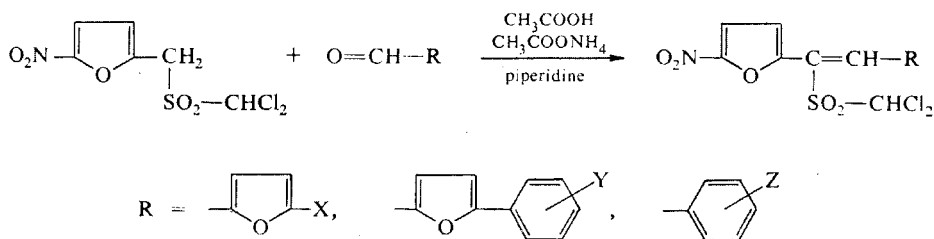
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Condensation of 5-nitrofurfuryl dichloromethyl sulphone (*IV*) with corresponding aromatic and heterocyclic aldehydes afforded 1-(5-nitro-2-furyl)-1-dichloromethylsulphonyl-2-(5-X-furyl)ethylenes *I*, 1-(5-nitro-2-furyl)-1-dichloromethylsulphonyl-2-[5-(Y-phenyl)-2-furyl]ethylenes *II* and 1-(5-nitro-2-furyl)-1-dichloromethylsulphonyl-2-(Z-phenyl)ethylenes *III*, where X = H, CH<sub>3</sub>, SCH<sub>3</sub>, Cl, Br, I, COOCH<sub>3</sub>, NO<sub>2</sub>; Y = H, 4-CH<sub>3</sub>, 2-Cl, 4-Cl, 3,4-Cl<sub>2</sub>, 4-Br, 4-COOC<sub>2</sub>H<sub>5</sub>, 2-NO<sub>2</sub>, 3-NO<sub>2</sub>, 3-NO, and Z = H, 4-CH<sub>3</sub>, 3-OCH<sub>3</sub>, 4-NHCOCH<sub>3</sub>, 2-F, 4-F, 2-Cl, 4-Cl. The UV and IR spectra of these  $\alpha,\beta$ -unsaturated sulphones are interpreted.

Our previous papers<sup>1-4</sup> dealt with preparation of various  $\alpha,\beta$ -unsaturated sulphones of 5-nitrofuran series. In this study we report the synthesis of compounds *I-III* by a one-step condensation of *IV* with 5-substituted-2-furaldehydes *V*, arylfuraldehydes *VI* and benzaldehydes *VII*. The condensations were carried out in glacial acetic acid, using ammonium acetate and piperidine as catalysts, according to Scheme 1:



SCHEME 1

Physical constants of the prepared compounds, together with their UV and IR spectral data, are listed in Tables I and II. All these compounds exhibit a narrow absorption band in the region  $900-896 \text{ cm}^{-1}$  which is characteristic for a furan nu-

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cleus<sup>5</sup>. As seen from Table II, the substituents have practically no influence on the position of the characteristic  $\nu(\text{NO}_2)$  and  $\nu(\text{SO}_2)$  absorption bands. Generally, the  $\nu(\text{NO}_2)_{\text{as}}$  band in the spectra of compounds *III* is strongly shifted to lower wavenumbers as compared with the spectra of compounds *I* and *II*.

The most important band for structural considerations, and particularly for the question of the capability of existence of the system in a planar conformation, is the last UV-absorption band, so called K-band, corresponding to electron transitions of the whole system<sup>6</sup>.

The absorption curves of 1-(5-nitro-2-furyl)-2-arylethylenes(*a,b*) and 1-(5-nitro-2-furyl)-1-dichloromethylsulphonyl-(2-substituted)ethylenes(*c,d,e*) are depicted in Figs 1 and 2. A comparison of the K-band of compound *a* with the K bands of compounds *c* and *d*, as well as of K band of *b* with that of *e* shows that the planar systems *a* and *b* exhibit very strong absorption bands, extending to the visible region, whereas the last band in the spectra of trisubstituted ethylenes *c*, *d* and *e* is very weak and is shifted several tens of nm to higher wavenumbers.

On the basis of these spectral data we can conclude that the molecules of the studied compounds are not planar. This conclusion is in accord with an analysis using molecular models, as well as with the literature data<sup>1-3</sup>.

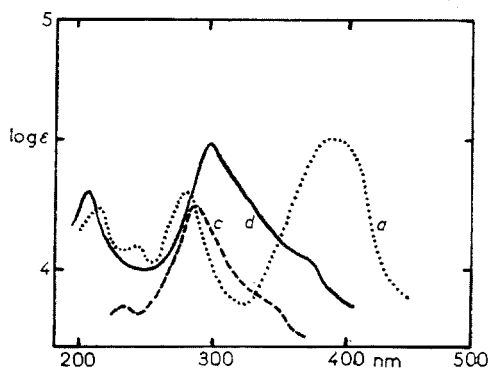


FIG. 1

UV Spectra of 1-(5-Nitro-2-furyl)-2-phenylethylene (*a*), 1-(5-Nitro-2-furyl)-1-dichloromethylsulphonyl-2-phenylethylene (*c*) and 1-(5-Nitro-2-furyl)-1-dichloromethylsulphonyl-2-furylethylene (*d*)

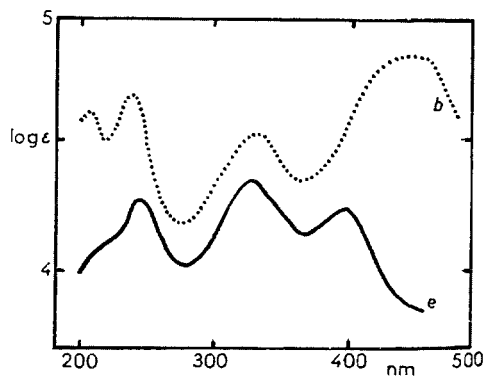


FIG. 2

UV Spectra of 1-(5-Nitro-2-furyl)-2-(5-phenyl-2-furyl)-ethylene (*b*) and 1-(5-Nitro-2-furyl)-1-dichloromethylsulphonyl-2-(5-phenyl-2-furyl)-ethylene (*e*)

TABLE I  
 $\alpha,\beta$ -Unsaturated Sulphones

Compound X Y Z	M.p., °C (yield, %)	Formula (mol.w.)	Calculated/Found			
			% C	% H	% N	% S
1-(5-Nitro-2-furyl)-1-dichloromethylsulphonyl-2-(5-X-furyl)ethylenes						
<i>VIII</i>	134—135	$C_{11}H_7Cl_2NO_6S$	37.69	1.99	4.01	9.14
H	(42)	(351.3)	37.61	1.92	4.02	9.21
<i>IX</i>	123—125	$C_{12}H_9Cl_2NO_6S$	39.45	2.46	3.86	8.76
CH <sub>3</sub>	(38)	(365.1)	39.38	2.52	3.81	8.89
<i>X</i>	131—132	$C_{12}H_9Cl_2NO_6S_2$	26.27	2.26	3.53	16.12
SCH <sub>3</sub>	(47)	(397.2)	36.21	2.19	3.71	16.24
<i>XI</i>	127—128	$C_{11}H_6Cl_3NO_6S$	37.40	1.96	3.96	9.06
Cl	(40)	(353.2)	37.49	1.91	4.12	8.85
<i>XII</i>	125—126	$C_{11}H_6BrCl_2NO_6S$	30.75	1.39	3.25	7.44
Br	(54)	(430.6)	30.59	1.43	3.36	7.25
<i>XIII</i>	117—118	$C_{11}H_6Cl_2INO_6S$	27.61	1.26	2.93	6.71
I	(41)	(477.1)	27.58	1.27	2.90	6.75
<i>XIV</i>	172—173	$C_{13}H_9Cl_2NO_8S$	37.10	2.19	3.42	7.84
COOCH <sub>3</sub>	(52)	(409.3)	37.17	2.24	3.60	7.91
<i>XV</i>	135—136	$C_{11}H_6Cl_2N_2O_8S$	33.32	1.53	7.08	8.08
NO <sub>2</sub>	(40)	(396.5)	33.37	1.59	7.10	8.02
1-(5-Nitro-2-furyl)-1-dichloromethylsulphonyl-2-[5-(Y-phenyl)-2-furyl]ethylenes						
<i>XVI</i>	137—138	$C_{17}H_{11}Cl_2NO_6S$	47.70	2.57	3.28	7.50
H	(45)	(428.2)	47.73	2.51	3.29	7.45
<i>XVII</i>	165—166	$C_{18}H_{13}Cl_2NO_6S$	48.98	2.95	3.17	7.25
4 CH <sub>3</sub>	(52)	(441.6)	48.88	2.99	3.20	6.99
<i>XVIII</i>	151—152	$C_{17}H_{10}Cl_3NO_6S$	44.25	2.17	3.03	6.94
2-Cl	(53)	(461.8)	44.29	2.11	3.02	6.84
<i>XIX</i>	225—226	$C_{17}H_{10}Cl_3NO_6S$	44.25	2.17	3.03	6.94
4-Cl	(49)	(461.8)	44.32	2.19	3.42	6.50
<i>XX</i>	190—191	$C_{17}H_9Cl_4NO_7S$	41.21	1.82	2.82	6.46
3,4-Cl <sub>2</sub>	(42)	(495.3)	41.16	1.90	2.88	6.36
<i>XXI</i>	163—164	$C_{17}H_{10}BrCl_2NO_6S$	40.32	1.98	2.87	6.33
4-Br	(50)	(506.4)	40.27	1.90	2.76	6.32
<i>XXII</i>	160—161	$C_{20}H_{15}Cl_2NO_8S$	48.10	3.01	2.80	6.41
4-COOC <sub>2</sub> H <sub>5</sub>	(51)	(499.3)	48.19	3.05	2.82	6.38

TABLE I  
 (Continued)

Compound X Y Z	M.p., °C (yield, %)	Formula (mol.w.)	Calculated/Found			
			% C	% H	% N	% S
<i>XXIII</i> 2-NO <sub>2</sub>	140–141 (45)	C <sub>17</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>8</sub> S (472·2)	43·22 43·10	2·12 2·19	5·93 6·02	6·78 6·68
<i>XXIV</i> 3-NO <sub>2</sub>	210–212 (48)	C <sub>17</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>8</sub> S (472·2)	43·22 43·18	2·12 2·11	5·93 5·98	6·78 6·57
<i>XXV</i> 4-NO <sub>2</sub>	151–152 (44)	C <sub>17</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>8</sub> S (472·2)	43·22 43·16	2·12 2·18	5·93 7·77	6·78 6·97
1-(5-Nitro-2-furyl)-1-dichloromethylsulphonyl-2-(Z-phenyl)ethylenes						
<i>XXVI</i> H	112–113 (20)	C <sub>13</sub> H <sub>9</sub> Cl <sub>2</sub> NO <sub>5</sub> S (361·2)	42·05 41·91	2·49 2·41	3·77 3·79	8·62 8·69
<i>XXVII</i> 4-CH <sub>3</sub>	129–130 (24)	C <sub>14</sub> H <sub>11</sub> Cl <sub>2</sub> NO <sub>5</sub> S (375·0)	44·80 44·73	2·93 2·95	3·73 3·75	8·53 8·54
<i>XXVIII</i> 3-OCH <sub>3</sub>	114–115 (23)	C <sub>14</sub> H <sub>11</sub> Cl <sub>2</sub> NO <sub>6</sub> S (391·4)	42·97 42·89	2·82 2·75	3·58 3·53	8·18 8·15
<i>XXIX</i> 4-NHCOOH <sub>3</sub>	140–141 (24)	C <sub>15</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>6</sub> S (418·2)	43·06 43·01	2·87 2·81	6·69 6·37	7·65 7·89
<i>XXX</i> 2-F	86–87 (21)	C <sub>13</sub> H <sub>8</sub> Cl <sub>2</sub> FNO <sub>5</sub> S (379·1)	41·15 41·19	2·11 2·10	3·69 3·72	8·44 8·46
<i>XXXI</i> 4-F	89–91 (19)	C <sub>13</sub> H <sub>8</sub> Cl <sub>2</sub> FNO <sub>5</sub> S (379·1)	41·16 41·14	2·11 2·13	3·69 3·71	8·44 8·45
<i>XXXII</i> 2-Cl	145–147 (21)	C <sub>13</sub> H <sub>8</sub> Cl <sub>3</sub> NO <sub>5</sub> S (395·3)	39·49 39·40	2·02 2·08	3·54 3·62	8·10 7·84
<i>XXXIII</i> 4-Cl	137–138 (23)	C <sub>13</sub> H <sub>8</sub> Cl <sub>3</sub> NO <sub>5</sub> S (395·3)	39·49 39·45	2·02 2·10	3·54 3·52	8·10 8·02

TABLE II  
UV and IR Spectra of  $\alpha,\beta$ -Unsaturated Sulphones

Compound X Y Z	$\lambda_{\max}$ , nm <sup>a</sup> (log $\epsilon$ )			$\tilde{\nu}$				
				(NO <sub>2</sub> ) <sub>as</sub>	(NO <sub>2</sub> ) <sub>s</sub>	(SO <sub>2</sub> ) <sub>as</sub>	(SO <sub>2</sub> ) <sub>s</sub>	
1-(5-Nitro-2-furyl)-1-dichlorosulphonyl-2-(5-X-furyl)ethylenes								
<i>VIII</i> H	243 (3·87)	304 (4·49)	i377 (4·07)	1 548	1 359	1 324	1 150	
<i>IX</i> CH <sub>3</sub>	234 (3·90)	311 (4·48)	i393 (4·08)	1 547	1 357	1 320	1 151	
<i>X</i> SCH <sub>3</sub>	227 (4·11)	326 (4·27)	402 (4·10)	1 549	1 357	1 326	1 150	
<i>XI</i> Cl	236 (3·80)	306 (4·44)	i371 (4·04)	1 542	1 358	1 321	1 150	
<i>XII</i> Br	232 (3·80)	309 (4·40)	i375 (4·01)	1 547	1 359	1 321	1 151	
<i>XIII</i> I	243 (3·92)	313 (4·42)	r366 (4·12)	1 540	1 358	1 321	1 154	
<i>XIV</i> COOCH <sub>3</sub>	213 (4·18)	303 (4·48)	i370 (3·97)	1 549	1 359	1 318	1 154	
<i>XV</i> NO <sub>2</sub>	243 (4·12)	308 (4·41)	371 (4·08)	1 554	1 358	1 324	1 154	
1-(5-Nitro-2-furyl)-1-dichlorosulphonyl-2-[(Y-phenyl)-2-furyl]ethylenes								
<i>XVI</i> H	i210 (3·99)	246 (4·28)	328 (4·47)	398 (4·27)	1 559	1 358	1 322	1 150
<i>XVII</i> 4-CH <sub>3</sub>	211 (4·08)	250 (4·19)	330 (4·29)	412 (4·19)	1 558	1 357	1 321	1 150
<i>XVIII</i> 2-Cl	214 (4·12)	251 (4·27)	332 (4·39)	426 (4·25)	1 556	1 359	1 321	1 150
<i>XIX</i> 4-Cl	215 (4·14)	280 (4·29)	341 (4·28)	427 (4·26)	1 559	1 356	1 320	1 150
<i>XX</i> 3,4-Cl <sub>2</sub>	216 (4·20)	248 (4·21)	324 (4·33)	397 (4·20)	1 557	1 355	1 321	1 150
<i>XXI</i> 4-Br	205 (4·31)	257 (4·26)	328 (4·39)	405 (4·27)	1 558	1 357	1 320	1 150
<i>XXII</i> 4-COOC <sub>2</sub> H <sub>5</sub>	r210 (4·01)	256 (4·29)	326 (4·38)	402 (4·27)	1 557	1 358	1 320	1 150

TABLE II  
 (Continued)

Compound X Y Z	$\lambda_{\max}$ , nm <sup>a</sup> (log $\epsilon$ )				$\tilde{\nu}$			
					(NO <sub>2</sub> ) <sub>as</sub>	(NO <sub>2</sub> ) <sub>s</sub>	(SO <sub>2</sub> ) <sub>as</sub>	(SO <sub>2</sub> ) <sub>s</sub>
<i>XXIII</i> 2-NO <sub>2</sub>	r211 (4·17)	244 (4·26)	315 (4·42)	383 (4·18)	1 558	1 359	1 322	1 152
<i>XXIV</i> 3-NO <sub>2</sub>	i212 (4·07)	244 (4·37)	323 (4·38)	389 (4·18)	1 560	1 358	1 322	1 150
<i>XXV</i> 4-NO <sub>2</sub>	204 (4·31)	251 (4·29)	328 (4·37)	405 (4·26)	1 559	1 358	1 322	1 150
1-(5-Nitro-2-furyl)-1-dichlorosulphonyl-2-(Z-phenyl)ethylenes								
<i>XXVI</i> H	207 (4·41)	i219 (4·21)	287 (4·26)	—	1 510	1 360	1 320	1 150
<i>XXVII</i> 4-CH <sub>3</sub>	205 (4·29)	r226 (4·19)	298 (4·38)	—	1 510	1 360	1 320	1 151
<i>XXVII</i> 4-CH <sub>3</sub>	205 (4·29)	r226 (4·19)	298 (4·38)	—	1 510	1 360	1 320	1 151
<i>XXVIII</i> 3-OCH <sub>3</sub>	206 (4·47)	—	289 (4·25)	—	1 510	1 360	1 318	1 150
<i>XXIX</i> 4-NHCOCH <sub>3</sub>	—	230 (4·19)	310 (4·49)	—	1 510	1 360	1 319	1 152
<i>XXX</i> 2-F	207 (4·31)	—	287 (4·18)	—	1 510	1 361	1 310	1 150
<i>XXXI</i> 4-F	207 (4·29)	—	292 (4·26)	—	1 510	1 360	1 314	1 152
<i>XXXII</i> 2-Cl	207 (4·40)	—	292 (4·13)	—	1 510	1 359	1 318	1 150
<i>XXXIII</i> 4-Cl	206 (4·29)	i226 (4·21)	297 (4·24)	—	1 510	1 360	1 319	1 150

<sup>a</sup> i Inflex, r shoulder.

## EXPERIMENTAL

### 5-Nitrofurfuryl Dichloromethyl Sulphone (*IV*)

Sodium bromide (9 g; 0.087 mol) was added to a solution of 5-nitrofurfuryl nitrate (15 g; 0.08 mol) in ethanol (200 ml), the mixture was refluxed for 2 hours, cooled to 60°C and a suspension of sodium dichloromethanesulphinat (15.5 g; 0.09 mol) in ethanol (250 ml) was added under stirring. The mixture was heated to 60°C for 2 hours and refluxed for 1 hour. The ethanol is distilled off and the residue was extracted with ether (150 ml). Light petroleum (300 ml) was added to the stirred ethereal extract and stirring was continued for 30 min. The separated product was filtered, m.p. 71–73°C yield 3.2 g (54%). When dimethylformamide was used as the reaction medium, the reaction mixture was poured on ice and the product was isolated as described above<sup>7</sup>.

### Preparation of Compounds *I–III*

A mixture of *IV* (0.01 mol), the corresponding aldehyde *V–VII* (0.011 mol), piperidine (0.2 g), ammonium acetate (1.5 g) and glacial acetic acid (40 ml) was refluxed for 2 h, cooled and poured on crushed ice (100 g) under stirring. The crude product was filtered, washed with water, dried and crystallized from ethanol or dimethylformamide, or it was purified by chromatography<sup>8</sup>.

### Spectral Measurements

The IR spectra were taken on a Zeiss (Jena) UR-20 spectrophotometer in chloroform from which ethanol was removed by passing twice through a column packed with blue silica gel. The instrument was calibrated by polystyrene foil. The measurements were carried out in NaCl cells (0.02 to 1 mm) in saturated or 0.02M chloroform solutions. The electronic absorption spectra were measured in ethanol on a Specord UV VIS Zeiss recording spectrophotometer, concentration 2.5 to 5.0 · 10<sup>-5</sup>M, cell thickness 1 cm, accuracy ± 1 nm.

### REFERENCES

1. Jurášek A., Kováč J.: This Journal 38, 1705 (1973).
2. Jurášek A., Kováč J., Geisbacher D.: This Journal 39, 1220 (1974).
3. Jurášek A., Kováč J., Abrahám J.: Chem. Zvesti 28, 262 (1974).
4. Hrdina M., Jurášek A., Frimm R.: Chem. Zvesti 28, 418 (1974).
5. Nakanishi K.: *Infrared Absorption Spectroscopy*, Russian translation. Mir, Moscow 1955.
6. Brand J. C. D., Eglinton G.: *Application of Spectroscopy to Organic Chemistry*, Russian translation, p. 212. Mir, Moscow 1967.
7. Jurášek A., Hrdina M.: Czech. Appl. No 159 482 (7. 8. 1974).
8. Hrdina M., Jurášek A., Frimm R., Ebringer L.: Czech. Appl. No 164 654 (2. 6. 1975).

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