

# Reactions of substituted 2-(2-furyl)-1,1,2-ethylenetricarbonitriles with primary and secondary amines

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Received 3 June 1988

(5-Bromo-2-furyl)ethylenetricarbonitrile reacts with primary and secondary amines selectively under formation of *N*-substituted (5-amino-2-furyl)ethylenetricarbonitriles. In an analogous nucleophilic substitution of (5-nitro-2-furyl)ethylenetricarbonitrile, furan ring and the exocyclic double bond compete for the nucleophile. Consequently, nitriles of the 3-(*N*-alkylamino)-2-cyano-3-(5-nitro-2-furyl)propenoic acid are also formed. Several spectral characteristics of the prepared compounds are discussed.

(5-Бром-2-фурил)этиленстрикарбонитрил взаимодействует с первичными и вторичными аминами селективно с образованием *N*-замещенных (5-амино-2-фурил)этиленстрикарбонитрилов. При аналогичном нуклеофильном замещении (5-нитро-2-фурил)этиленстрикарбонитрила имеет место конкуренция по сродству к нуклеофилу между фурановым циклом и экзоциклической двойной связью. Вследствие этого образуются также нитрилы 3-(*N*-алкиламино)-2-циано-3-(5-нитро-2-фурил)акриловой кислоты. Обсуждаются некоторые спектральные характеристики полученных соединений.

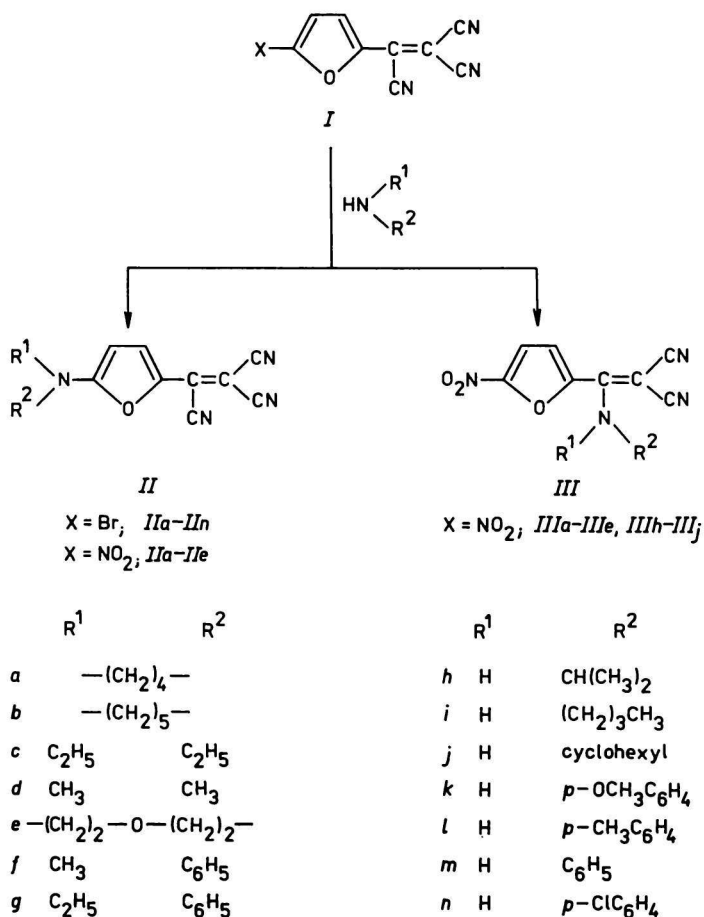
Nucleophilic substitutions have so far been usually studied on 2,5-disubstituted furan models, possessing various activating electron-withdrawing groups [1]. Detailed studies were conducted especially with secondary amines [2–5]. Products of nucleophilic substitution with primary aliphatic amines on the other hand could not yet been isolated [6]. Reactions with substituted anilines were successful only in the case of the derivatives of 5-(*N*-phenylamino)-2-furfurylidene-*N*-phenyliminium halides [3, 7, 8].

In the present paper we describe the reactivity of 2-(5-*X*-2-furyl)-1,1,2-ethylenetricarbonitriles (*Ia*: *X* = Br; *Ib*: *X* = NO<sub>2</sub>) in their reactions with primary and secondary amines. In contrast to the previously studied furan derivatives [1–5], compounds *Ia*, *Ib* incorporate in their molecules the so far strongest (in the furan series) tricyanovinyl activating group ( $\sigma_p = 1.70$ ) [9]. That allowed for the first time to isolate even the products of nucleophilic substitution of primary aliphatic amines at the furan ring.

In spite of strong activation 2-(5-bromo-2-furyl)ethylenetricarbonitrile (*Ia*) [10] reacted selectively with the amines under study. Both alkylamines, primary

and secondary anilines gave in high yields the *N*-substituted 2-(5-amino-2-furyl)ethylenetricarbonitriles *IIa—IIh* (Scheme 1, Table 1). Derivative *IIf* was prepared from the more accessible *N,N*-dimethylaniline *via* an unstable ammonium salt, which after spontaneous demethylation gave directly *IIf*. Similar reaction has already been described in the series of trimethylammonium salts of furan [11]. The use of polar ethyl acetate as reaction medium not only accelerated the reaction itself, but facilitated the isolation of products *IIa—IIh* as well.

When the reaction substrate contained two powerful activating groups, such as those in 2-(5-nitro-2-furyl)ethylenetricarbonitrile (*Ib*) [12], both the position 5 of the furan ring and the tricyanovinyl group competed for the nucleophile



Scheme 1

Table 1

Physicochemical data of derivatives *IIa—IIg*

| Compound   | Formula<br>$M_r$                                 | $w_i(\text{calc.})/\%$ |      |      | Yield<br>%      | M.p.<br>°C | $\lambda_{\text{max}}/\text{nm}$<br>( $\log \{\epsilon\}$ ) | $\tilde{\nu}(\nu(\text{C}\equiv\text{N}))/\text{cm}^{-1}$ |
|------------|--|------------------------|------|------|-----------------|------------|---|---|
|            |  | C                      | H    | N    |                 |            |   |   |
| <i>IIa</i> | $\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}$   | 65.5                   | 4.23 | 23.5 | 68              | 220—221    | 525, 496<br>(4.00, 3.76)                                    | 2182.5<br>2197.5  |
|            | 238.3  | 65.7                   | 4.29 | 23.4 |                 |            |   |   |
| <i>IIb</i> | $\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}$   | 66.6                   | 4.79 | 22.2 | 80              | 225—227    | 527, 498<br>(3.96, 3.71)                                    | 2188<br>2198.5  |
|            | 252.3  | 66.7                   | 4.87 | 22.3 |                 |            |   |   |
| <i>IIc</i> | $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}$   | 65.0                   | 5.03 | 23.3 | 75              | 173—175    | 527, 498<br>(3.66, 3.42)                                    | 2187<br>2197.5  |
|            | 240.3  | 65.0                   | 5.09 | 23.5 |                 |            |   |   |
| <i>IId</i> | $\text{C}_{11}\text{H}_8\text{N}_4\text{O}$      | 62.3                   | 3.80 | 26.4 | 75              | 231—233    | 532, 503<br>(3.60, 3.39)                                    | 2192  |
|            | 212.2  | 62.4                   | 3.84 | 26.3 |                 |            |   |   |
| <i>IIe</i> | $\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_2$ | 61.4                   | 3.96 | 22.0 | 79              | 241—243    | 526, 496<br>(3.89, 3.63)                                    | 2186<br>2199  |
|            | 254.3  | 61.5                   | 4.03 | 22.0 |                 |            |   |   |
| <i>IIf</i> | $\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}$   | 70.0                   | 3.68 | 20.4 | 72 <sup>a</sup> | 228—230    | 533, 503<br>(3.48, 3.26)                                    | 2180  |
|            | 274.3  | 70.0                   | 3.76 | 20.5 |                 |            |   |   |
| <i>IIg</i> | $\text{C}_{17}\text{H}_{12}\text{N}_4\text{O}$   | 70.8                   | 4.20 | 19.4 | 87              | 173—174    | 525, 502<br>(4.06, 3.83)                                    | 2204  |
|            | 288.3  | 70.9                   | 4.28 | 19.6 |                 |            |   |   |

Table 1 (Continued)

| Compound   | Formula<br>$M_r$                                 | $w_i(\text{calc.})/\%$<br>$w_i(\text{found})/\%$ |      |      | Yield<br>%          | M.p.<br>°C    | $\lambda_{\text{max}}/\text{nm}$<br>(log { $\epsilon$ }) | $\tilde{\nu}(\nu(\text{C}\equiv\text{N}))/\text{cm}^{-1}$ |
|------------|--|--|------|------|---------------------|---------------|--|---|
|            |  | C  | H    | N    |                     |               |  |   |
| <i>Iih</i> | $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}$   | 63.7   | 4.46 | 24.8 | 58                  | 203—205       | 516, 488<br>(3.72, 3.48)                                 | 2209  |
|            | 226.2  | 63.8   | 4.54 | 24.9 |                     |               |  |   |
| <i>Iii</i> | $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}$   | 65.0   | 5.03 | 23.3 | 45                  | 142—145       | 517, 485<br>(3.70, 3.46)                                 | 2195  |
|            | 240.3  | 65.5   | 5.09 | 22.9 |                     |               |  |   |
| <i>Iij</i> | $\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}$   | 67.7   | 5.30 | 21.0 | 60                  | 172—174       | 519, 490 <sup>b</sup><br>(4.21, 3.98)                    | 2190  |
|            | 266.3  | 67.8   | 5.41 | 21.2 |                     |               |  |   |
| <i>Iik</i> | $\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_2$ | 66.2   | 3.47 | 19.3 | 83                  | 210 (decomp.) | 543<br>(3.58)  | 2201  |
|            | 290.3  | 66.4   | 3.54 | 19.4 |                     |               |  |   |
| <i>Iil</i> | $\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}$   | 70.1   | 3.68 | 20.4 | 78, 44 <sup>c</sup> | 210 (decomp.) | 545<br>(3.44)  | 2203  |
|            | 274.3  | 70.2   | 3.78 | 20.6 |                     |               |  |   |
| <i>Iim</i> | $\text{C}_{15}\text{H}_8\text{N}_4\text{O}$      | 69.2   | 3.10 | 21.5 | 66                  | 240 (decomp.) | 537<br>(3.58)  | 2210  |
|            | 260.3  | 69.4   | 3.15 | 21.7 |                     |               |  |   |
| <i>Iin</i> | $\text{C}_{15}\text{H}_7\text{ClN}_4\text{O}$    | 61.1   | 2.39 | 19.0 | 75                  | 255 (decomp.) | 539<br>(3.63)  | 2216  |
|            | 294.7  | 61.5   | 2.42 | 19.2 |                     |               |  |   |

a) Reaction with  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ ; b) measured in acetone; c) from the reaction with *Ib* in dichloroethane.

Table 2

Physicochemical properties of compounds *IIIa—IIIe*, *IIIh—IIIj*

| Compound     | Formula<br>$M_r$                                 | $w_i(\text{calc.})/\%$<br>$w_i(\text{found})/\%$ |      |      | Yield<br>% | M.p.<br>°C  | $\lambda_{\text{max}}/\text{nm}$<br>( $\log \{\epsilon\}$ ) | $\tilde{\nu}(\nu(\text{C}\equiv\text{N}))/\text{cm}^{-1}$ |
|--------------|--|--|------|------|------------|-------------|---|---|
|              |  | C  | H    | N    |            |             |   |   |
| <i>IIIa</i>  | $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_3$ | 55.8   | 3.90 | 21.7 | 70         | 155.5—156.5 | 287<br>(3.60)   | 2189<br>2208  |
|              | 258.2  | 55.9   | 3.95 | 21.8 |            |             |   |   |
| <i>IIIb</i>  | $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_3$ | 57.4   | 4.44 | 20.6 | 26         | 126—128     | 288<br>(3.31)   | 2186<br>2208.5  |
|              | 272.3  | 57.4   | 4.49 | 20.7 |            |             |   |   |
| <i>IIIc</i>  | $\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_3$ | 55.4   | 4.65 | 21.5 | 12         | 168—170     | 287<br>(3.59)   | 2186<br>2205  |
|              | 260.3  | 56.5   | 4.69 | 21.5 |            |             |   |   |
| <i>III d</i> | $\text{C}_{10}\text{H}_8\text{N}_4\text{O}_3$    | 51.7   | 3.47 | 24.1 | 28         | 195.0—196.5 | 285<br>(3.34)   | 2186<br>2186  |
|              | 232.2  | 51.8   | 3.51 | 24.1 |            |             |   |   |
| <i>IIIe</i>  | $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_4$ | 52.6   | 3.68 | 20.4 | 7          | 176—177     | 292<br>(3.36)   | 2186<br>2209  |
|              | 274.2  | 52.6   | 3.75 | 20.3 |            |             |   |   |
| <i>IIIh</i>  | $\text{C}_{11}\text{H}_{10}\text{N}_4\text{O}_3$ | 53.7   | 4.09 | 22.8 | 74         | 154—155     | 286, 350<br>(3.29, 3.00)                                    | 2206<br>2206  |
|              | 246.2  | 53.8   | 4.17 | 22.9 |            |             |   |   |
| <i>IIIi</i>  | $\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_3$ | 55.4   | 4.65 | 21.5 | 80         | 70—73       | 291, 355<br>(3.21, 2.90)                                    | 2222<br>2212  |
|              | 260.3  | 55.9   | 4.73 | 21.8 |            |             |   |   |
| <i>IIIj</i>  | $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_3$ | 58.7   | 4.93 | 19.6 | 69         | 173—175     | 289, 351<br>(3.27, 2.95)                                    | 2200<br>2210  |
|              | 289.3  | 58.9   | 4.99 | 19.7 |            |             |   |   |

(Scheme 1). Thus the resulting reaction mixtures (with secondary amines) contained beside derivatives *Ila—Ile* (yields are given in Experimental) also the nitriles of 3-(*N,N*-dialkylamino)-2-cyano-3-(5-nitro-2-furyl)propenoic acid *IIIa—IIIe* (Table 2).

In the indicated series of the utilized secondary amines morpholine, diethylamine, piperidine, dimethylamine, pyrrolidine the ratio *III/II* gradually increased. Primary amines attacked predominantly the tricyanovinyl group and gave derivatives *IIIh—IIIj* (Table 2). Substitution of the nitro group at the furan ring, a minor reaction, led to the formation of derivatives *IIIh—IIIj* in yields under 5%. Reaction of *Ib* with anilines gave a complex mixture of products, some of which could possibly have arisen by the ion radical mechanism [12] (Table 1).

Prepared *N*-substituted derivatives *Ila—Iln* are stable compounds, forming crystals with metallic shine. Their UV maxima are, compared to other known derivatives of 2-furylethylenetricarbonitrile [10, 12, 13], strongly bathochromically shifted ( $\lambda_{\max} = 516\text{—}545\text{ nm}$ ;  $\log\{\varepsilon\} = 3.44\text{—}5.21$ ), quite what one would expect of compounds with such pronounced  $\pi$ -electron delocalization, indicated in the dipolar mesomeric structure (Scheme 2).



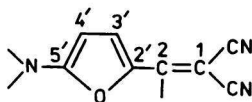
Scheme 2

High degree of intramolecular charge transfer was indicated also by  $^{13}\text{C}$  NMR spectra. Taking the unsubstituted 2-(2-furyl)ethylenetricarbonitrile (*Ic*) as a reference, compounds *II* had their C-1 significantly high-field shifted ( $\Delta\delta(\text{C-1}) \geq 25\text{ ppm}$ ) (Table 3). Chemical shift values of C-1 carbons correspond to those of analogous compounds *III* and are comparable with values published for push-pull substituted butadienes [14, 15].

Charge transfer across the furan ring is also manifested by the increased coupling constants  $^3J_{3,4}$  in  $^1\text{H}$  NMR spectra (Tables 4 and 5). The measured values ( $^3J_{3,4} = 4.8\text{—}4.9\text{ Hz}$ ) approach those in highly delocalized systems of pentamethinium salts of furan [8], or in the extreme case that of  $\gamma$ -ylidene- $\alpha,\beta$ -butenolide [16] ( $^3J_{3,4} = 5.0\text{—}5.5\text{ Hz}$ ). Structurally related 5-dialkylamino-2-furylylideneprapanedinitriles showed lower coupling constants ( $^3J_{3,4} = 4.0\text{ Hz}$ ) [4].

Based on the above-discussed spectral characteristics we have classified the prepared 2-(5-amino-2-furyl)ethylenetricarbonitriles *Ila—Iln* as polarized systems with significant push-pull stabilization, brought about by the conjugation

Table 3

<sup>13</sup>C NMR chemical shifts of selected derivatives

| Compound                  | $\delta$ /ppm |       |       |       |       |       |                         |   |
|---------------------------|---------------|-------|-------|-------|-------|-------|-------------------------|---|
|                           | C-1           | C-2   | C-2'  | C-3'  | C-4'  | C-5'  | CN                      | Others                                  |
| <i>Ic</i> <sup>a</sup>    | 85.6          | 127.2 | 147.2 | 126.6 | 116.7 | 153.3 | 113.1<br>112.9<br>112.3 | —                                       |
| <i>Iic</i>                | 56.6          | 113.9 | 142.8 | 136.3 | 100.7 | 167.0 | 117.0<br>116.4<br>116.2 | 45.7 13.8                               |
| <i>Iig</i>                | 60.0          | 113.7 | 142.5 | 135.9 | 101.1 | 166.8 | 116.4<br>115.9<br>115.9 | 49.2 14.0<br>140.6 131.1<br>129.8 127.3 |
| <i>Iih</i>                | 57.2          | 114.7 | 142.5 | 136.6 | 101.0 | 167.5 | 117.0<br>116.5<br>114.1 | 47.9 22.9                               |
| <i>Iik</i> <sup>b</sup>   | 53.8          | 116.7 | 142.5 | 135.7 | 104.4 | 162.9 | 113.7<br>113.8<br>111.8 | 129.0 114.7<br>122.4 157.2<br>55.4      |
| <i>Iie</i> <sup>b</sup>   | 55.2          | 116.3 | 142.3 | 135.2 | 104.0 | 162.8 | 113.6<br>113.6<br>112.5 | 135.7 130.0<br>120.5 133.5<br>20.4      |
| <i>Iim</i> <sup>a,b</sup> | —             | 116.6 | 142.5 | 135.6 | 104.7 | 162.7 | 113.8<br>113.8<br>111.7 | 126.7 120.9<br>129.5 125.4              |
| <i>IIIa</i> <sup>a</sup>  | —             | —     | 146.6 | 120.0 | 112.9 | 154.1 | 117.3<br>116.8          | 53.7 26.0                               |
| <i>IIIb</i>               | 54.5          | 157.4 | 146.1 | 122.4 | 113.0 | 154.4 | 117.0<br>116.2          | 54.0 27.2<br>23.9                       |
| <i>IIIc</i>               | 54.4          | 156.3 | 146.4 | 120.5 | 112.8 | 153.8 | 117.0<br>116.2          | 48.3 138                                |

a) Measured without the relaxation agent; b) measured in hexadeuterodimethyl sulfoxide.

of the amino group with the strongly electron-withdrawing tricyanovinyl group. This sort of stabilization allowed for the first time for the preparation of stable *N*-alkylaminofuran derivatives. The starting 2-(5-X-2-furyl)ethylenetricarbonitriles (*Ia*, *Ib*) constitute a novel type of reactive furan derivatives, capable of reactions, that were impossible to conduct with the hitherto known furans.

Table 4

<sup>1</sup>H NMR data of derivatives *IIa—IIn*

| Compound                | δ/ppm   |         |                      |  |
|-------------------------|---------|---------|----------------------|--|
|                         | H-3 (d) | H-4 (d) | J <sub>3,4</sub> /Hz | Others   |
| <i>IIa</i>              | 6.30    | 7.67    | 4.9                  | 3.83 (t, 4H, N—CH <sub>2</sub> ),<br>2.16 (t, 4H, CH <sub>2</sub> )  |
| <i>IIb</i>              | 6.48    | 7.70    | 4.85                 | 3.86 (s, 4H, N—CH <sub>2</sub> ),<br>1.23 (m, 6H, CH <sub>2</sub> )  |
| <i>IIc</i>              | 6.44    | 7.69    | 4.9                  | 3.78 (q, 4H, CH <sub>2</sub> ),<br>1.35 (t, 6H, CH <sub>3</sub> )  |
| <i>II d</i>             | 6.41    | 7.70    | 4.9                  | 3.45 (s, 6H, CH <sub>3</sub> )   |
| <i>IIe</i>              | 6.45    | 7.74    | 4.8                  | 3.76 (t, 4H, O—CH <sub>2</sub> ),<br>3.05 (t, 4H, N—CH <sub>2</sub> )  |
| <i>II f<sup>a</sup></i> | 6.19    | 7.84    | 4.9                  | 7.54 (s, 5H, C <sub>6</sub> H <sub>5</sub> ),<br>3.69 (s, 3H, CH <sub>3</sub> )  |
| <i>II g</i>             | 5.92    | 7.67    | 4.9                  | 4.10 (q, 2H, N—CH <sub>2</sub> ),<br>1.34 (t, 3H, CH <sub>3</sub> ),<br>7.59 (s, 5H, C <sub>6</sub> H <sub>5</sub> )                               |
| <i>II h</i>             | 6.23    | 7.68    | 4.8                  | 4.19 (m, 1H, N—CH),<br>1.38 (d, 6H, CH <sub>3</sub> )  |
| <i>II i<sup>a</sup></i> | 6.28    | 7.74    | 4.85                 | 3.48 (t, 2H, J = 6.6 Hz, N—CH <sub>2</sub> ),<br>1.2—1.6 (m, 4H, CH <sub>2</sub> —CH <sub>2</sub> ),<br>0.89 (t, 3H, J = 6.6 Hz, CH <sub>3</sub> ) |
| <i>II j</i>             | 6.20    | 7.65    | 4.8                  | 1.12—2.12 (m, 11H, cyclohexyl)   |
| <i>II k</i>             | 6.42    | 7.74    | 4.85                 | 7.60 (d, 2H, J = 9.2 Hz, H-3', H-5'),<br>3.82 (s, 3H, CH <sub>3</sub> )  |
| <i>III</i>              | 6.37    | 7.65    | 4.9                  | 7.21 (d, 2H, J = 8.3 Hz, H-3', H-5'),<br>7.46 (d, 2H, J = 8.3 Hz, H-2', H-6'),<br>2.32 (s, 3H, CH <sub>3</sub> )                                   |
| <i>II m<sup>a</sup></i> | 6.43    | 7.83    | 4.8                  | 7.2—7.6 (m, 5H, C <sub>6</sub> H <sub>5</sub> )  |
| <i>II n<sup>a</sup></i> | 6.43    | 7.83    | 4.85                 | 7.56 (d, 2H, J = 8.8 Hz, H-2', H-6'),<br>7.39 (d, 2H, J = 8.8 Hz, H-3', H-5')  |

a) Measured in hexadeuterodimethyl sulfoxide.

## Experimental

Melting points were determined with the Kofler hot stage. Infrared spectra were measured with the Specord IR-75 spectrophotometer (Zeiss, Jena) in KBr discs, UV spectra of methanol or acetone solutions of the compounds ( $c = 2 \times 10^{-5}$ — $5 \times 10^{-5}$  mol dm<sup>-3</sup>,  $\epsilon$  values in m<sup>2</sup> mol<sup>-1</sup>) were recorded with the Specord UV VIS (Zeiss, Jena) spectrophotometer. <sup>1</sup>H NMR spectra of hexadeuteroacetone or hexadeuterodimethyl sulfoxide solutions of the compounds were taken with the Jeol model FX-100 (100 MHz) and are reported relative to tetramethylsilane, used as internal



Table 5

<sup>1</sup>H NMR data of derivatives *IIIa*—*IIIe*, *IIIh*—*IIIj*

| Compound    | $\delta$ /ppm |         |               |   |
|-------------|---------------|---------|---------------|---|
|             | H-3 (d)       | H-4 (d) | $J_{3,4}$ /Hz | Others  |
| <i>IIIa</i> | 7.36          | 7.65    | 4.0           | 3.85 (bs, 4H, 2 × N—CH <sub>2</sub> ),<br>2.10 (bs, 4H, 2 × CH <sub>2</sub> )                                 |
| <i>IIIb</i> | 7.51          | 7.66    | 3.9           | 3.70 (bs, 4H, 2 × N—CH <sub>2</sub> ),<br>1.81 (m, 6H, 3 × CH <sub>2</sub> )                                  |
| <i>IIIc</i> | 7.42          | 7.67    | 3.85          | 3.70 (q, 4H, 2 × N—CH <sub>2</sub> ),<br>1.37 (t, 6H, 2 × CH <sub>3</sub> )                                   |
| <i>IIId</i> | 7.49          | 7.62    | 4.0           | 3.35 (s, 6H, 2 × N—CH <sub>3</sub> )  |
| <i>IIIe</i> | 7.56          | 7.69    | 4.0           | 3.67—4.00 (m, 8H, 4 × CH <sub>2</sub> )   |
| <i>IIIh</i> | 7.52          | 7.67    | 4.0           | 4.28 (m, 1H, N—CH),<br>1.38 (d, 6H, 2 × CH <sub>3</sub> )   |
| <i>IIIi</i> | 7.56          | 7.68    | 4.0           | 3.70 (m, 2H, N—CH <sub>2</sub> ),<br>1.18—1.88 (m, 2H, N—CH <sub>2</sub> ),<br>0.91 (t, 3H, CH <sub>3</sub> ) |
| <i>IIIj</i> | 7.46          | 7.77    | 4.0           | 8.38 (bs, 1H, NH)<br>0.87—2.00 (m, 11H, cyclohexyl)   |

standard. <sup>13</sup>C NMR spectra were recorded on the same spectrometer, operating at 25.04 MHz. Compounds were measured as hexadeuteroacetone solutions with tetramethylsilane as internal standard and Cr<sup>III</sup>(acac)<sub>3</sub> as relaxation agent.

2-(5-Bromo-2-furyl)-1,1,2-ethylenetricarbonitrile (*Ia*) was prepared according to Ref. [10], 2-(5-nitro-2-furyl)-1,1,2-ethylenetricarbonitrile (*Ib*) was prepared by nitration of 2-furyl-1,1,2-ethylenetricarbonitrile (*Ic*) [13], according to the procedure, described in [12].

#### *N*-Substituted 2-(5-amino-2-furyl)-1,1,2-ethylenetricarbonitriles *IIa*—*IIn*\*

A solution of the corresponding amine (2 mmol) in ethyl acetate (15 cm<sup>3</sup>) was dropwise added to the stirred ethyl acetate solution (15 cm<sup>3</sup>) of *Ia* (0.25 g; 1 mmol) during 30 min. After the mixture was stirred for 1 h at room temperature, further 150 cm<sup>3</sup> of acetate were added, followed by an extraction with 3 × 50 cm<sup>3</sup> of water. Organic layer was dried with MgSO<sub>4</sub>, purified with charcoal and evaporated to dryness. The solid residue was crystallized from toluene—heptane mixture (volume ratio = 1 : 1) (Table 1).

\* Derivative *IIj* was prepared by the reaction with *N,N*-dimethylaniline.

*Nitriles of 3-amino-2-cyano-3-(5-nitro-2-furyl)propenoic acid*  
*IIIa—IIIe, IIIh—IIIj*

The respective dichloromethane solutions (15 cm<sup>3</sup>) of *Ib* (0.214 g; 1 mmol) and amine (2 mmol) were mixed and stirred for 30 min at laboratory temperature. The mixture was then evaporated to dryness and the residue chromatographed on silica gel, eluant toluene—ethyl acetate (volume ratio = 1 : 1). Isolated products were dried in vacuum and crystallized.

Physicochemical constants of derivatives *IIIa—IIIe*, *IIIh—IIIj* are given in Table 2. Yields (%) of *II* were the following: *Ila* 13, *Ilb* 62, *Ilc* 52, *Ild* 50, *Ile* 82.

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Translated by P. Zálupský