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Twofold Photochemical Dehydrocyclization Reaction of Substituted 2,5–Distyrylthiophenes and 2,5–Distyrylfurans

Miroslav Bajić, Grace M. Karminski-Zamola and Nikola Blažević*

Department of Organic Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, 41000 Zagreb, Croatia

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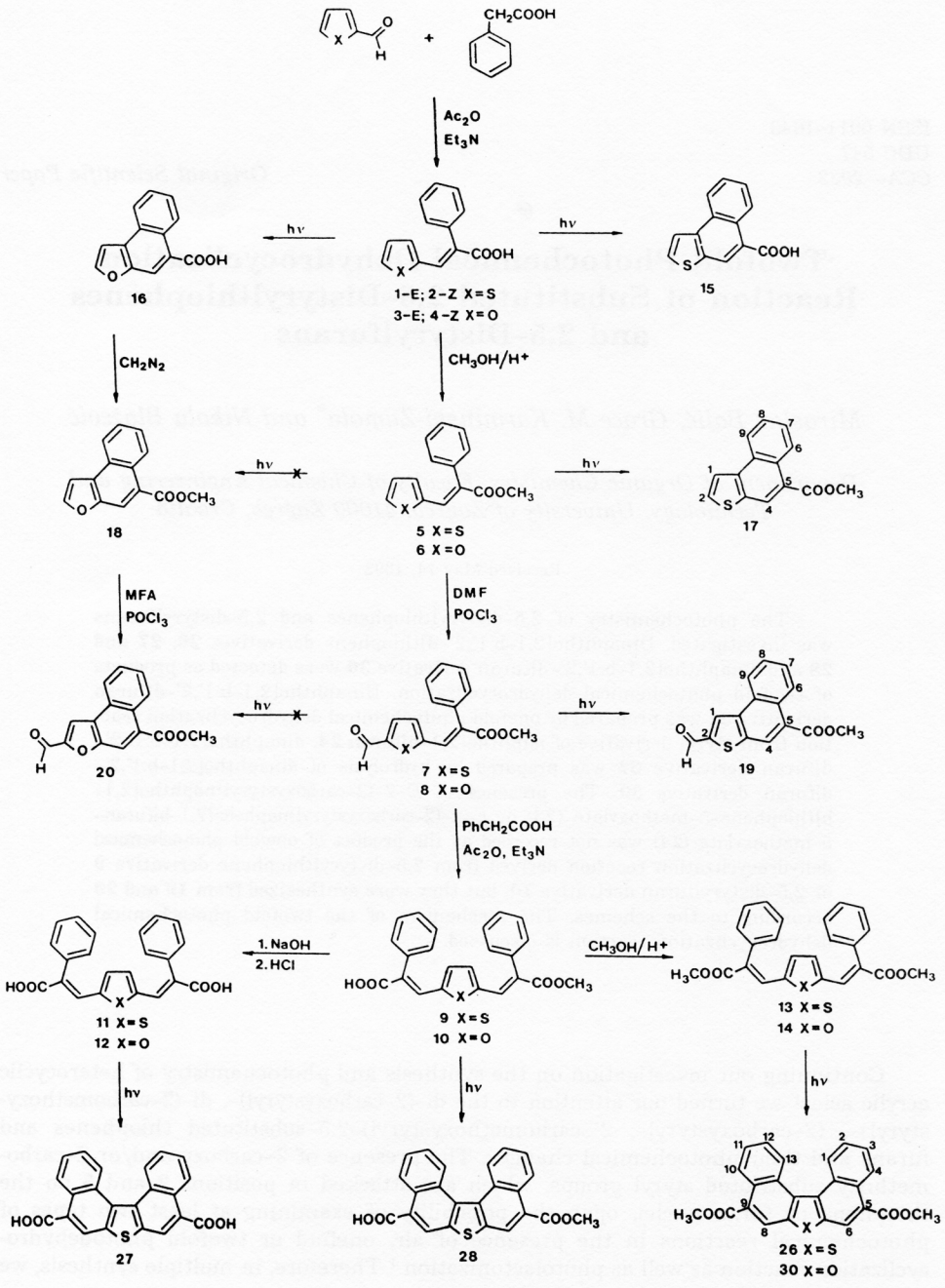
The photochemistry of 2,5–distyrylthiophenes and 2,5–distyrylfurans was investigated. Dinaphtho[2,1–b:1',2'–d]thiophene derivatives **26, 27** and **28** and dinaphtho[2,1–b:1',2'–d]furan derivative **30** were detected as products of twofold photochemical dehydrocyclization. Dinaphtho[2,1–b:1',2'–d]furan derivative **31** was prepared by onefold photochemical dehydrocyclization reaction from styryl derivative of naphtho[2,1–b]furan **24**, dinaphtho[2,1–b:1',2'–d]furan derivative **32** was prepared by hydrolysis of dinaphtho[2,1–b:1',2'–d]furan derivative **30**. The presence of *E*–2–(2–carboxystyryl)naphtho[2,1–b]thiophene–5–methoxylate (**23**) or *E*–2–(2–carboxystyryl)naphtho[2,1–b]furan–5–methoxylate (**24**) was not recorded as the product of onefold photochemical dehydrocyclization reaction derived from 2,5–distyrylthiophene derivative **9** or 2,5–distyrylfuran derivative **10**, but they were synthesized from **19** and **20** according to the schemes. The mechanism of the twofold photochemical dehydrocyclization reaction is discussed.

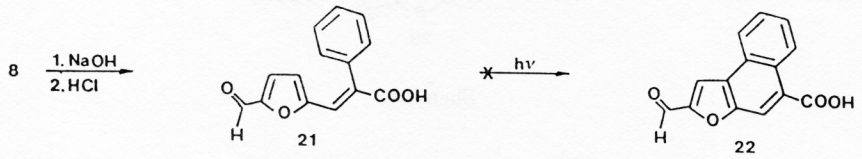
Continuing our investigation on the synthesis and photochemistry of heterocyclic acrylic acids[1] we turned our attention to the di–(2–carboxystyryl)–, di–(2–carbomethoxystyryl)–, (2–carboxystyryl–, 2'–carbomethoxystyryl)–2,5–substituted thiophenes and furans and their photochemical changes. The presence of 2–carboxy and/or 2–carbomethoxy substituted styryl groups, which are attacked in positions 2 and 5 on the thiophene or furan nuclei, open the possibility of examining at least two types of photochemical reactions in the presence of air, onefold or twofold photodehydrocyclization reaction as well as photolactonization.[1] Therefore, in multiple synthesis, we

* Author to whom correspondence should be addressed.


CH2COOH
Ac2O
Et3N
hν
COOH
1-E; 2-Z X=S
3-E; 4-Z X=O
16
15
CH2N2
CH3OH/H+
COOCH3
18
5 X=S
6 X=O
17
MFA
POCl3
DMF
POCl3
20
7 X=S
8 X=O
19
PhCH2COOH
Ac2O, Et3N
1. NaOH
2. HCl
CH3OH/H+
HOOC
H3COOC
11 X=S
12 X=O
9 X=S
10 X=O
13 X=S
14 X=O
27
28
26 X=S
30 X=O

Sheme 1.

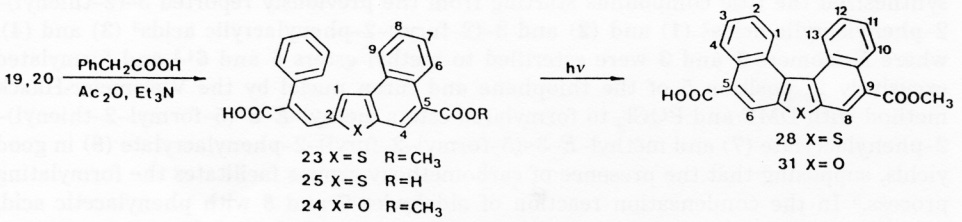
synthesized the title compounds starting from the previously reported 3–(2–thienyl)–2–phenylacrylic acids[2] (**1**) and (**2**) and 3–(2–furyl)–2–phenylacrylic acids[3] (**3**) and (**4**), where *E*–isomers **1** and **3** were esterified to methyl esters **5** and **6**[4,5] and formylated excusively in position 5 of the thiophene and furan nuclei by the Vielsmeier-Haack method with DMF and $POCl_3$ to formylated esters methyl–*E*–3–(5–formyl–2–thienyl)–2–phenylacrylate (**7**) and methyl–*E*–3–(5–formyl–2–furyl)–2–phenylacrylate (**8**) in good yields, supposing that the presence of carbomethoxy groups facilitates the formylating process.[5] In the condensation reaction of aldehydes **7** and **8** with phenylacetic acid, the title compounds were prepared: *E*–2–(2–carboxystyryl)–*E*–5–(2–carbomethoxystyryl)thiophene (**9**) in 27% yield and *E*–2–(2–carboxystyryl)–*E*–5–(2–carbomethoxystyryl)furan (**10**) in 61% yield. *Z*–isomers (or *E,Z* isomers) were obtained in traces. By hydrolysis of compounds **9** and **10** *E,E*–2,5–di–(2–carboxystyryl)thiophene (**11**) and *E,E*–2,5–di–(2–carboxystyryl)furan (**12**) were obtained, whereas esterification of **9** and **10** gave *E,E*–2,5–di–(2–carbomethoxystyryl)thiophene (**13**) and *E,E*–2,5–di–(2–carbomethoxystyryl)furan (**14**). At the same time, compounds **1** and **3** were photochemically dehydrocyclized into naphtho[2,1–b]thiophene–5–carboxylic acid (**15**) in 47% yield[2] and naphtho[2,1–b]furan–5–carboxylic acid (**16**) in 58% yield.[6] Methyl ester **5** was also successfully converted photochemically to naphtho[2,1–b]thiophene–5–methoxylate (**17**)[4] in 50% yield while the same reaction did not succeed in the furan series. However, naphtho[2,1–b]furan–5–methoxylate (**18**) was prepared from **16** by esterification with diazomethane. By photochemical irradiation of ester–aldehyde **7** in the cyclohexane solution 2–formyl–naphtho[2,1–b]thiophene–5–methoxylate (**19**) was prepared in 60% yield, but by irradiation of ester–aldehyde **8** under the same reaction conditions it was neither possible to isolate 2–formyl–naphtho[2,1–b]furan–5–methoxylate (**20**) nor formylacid **22** from 3–(5–formyl–2–furyl)–2–phenylacrylic acid (**21**) (see Scheme 2), although photochemical dehydrocyclization reaction of some formyl substituted difurylethenes has been reported.[7]



Sheme 2.

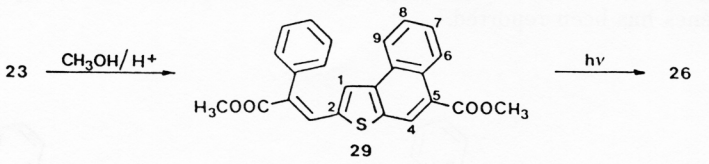
Ester–aldehyde **20** was prepared by formylation of **18** with methylformanilide and $POCl_3$. Aldehyde–esters **19** and **20** are the intermediates necessary for preparing *E*–2–(2–carboxystyryl)naphtho[2,1–b]thiophene–5–methoxylate (**23**) and *E*–2–(2–carboxystyryl)naphtho[2,1–b]furan–5–methoxylate (**24**), which were prepared by the condensation of **19** and **20** with phenylacetic acid (see Scheme 3).

Diacid **25** was also obtained during the process of isolation. The stereochemistry of compounds **23**, **25** and **24** was exclusively *E*. Compounds **23** and **24** served for examining the mechanism of the reaction.



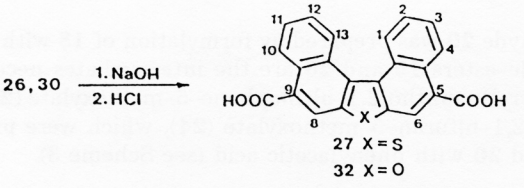
Sheme 3.

In this work, the process of twofold photochemical dehydrocyclization reaction was investigated, so that our attention was focussed on the isolation and detection of dinaphthothiophene and dinaphthofuran products. Distyrylthiophenes **9**, **11**, **13** and distyrylfurans **10**, **12** and **14** were exposed to UV irradiation in the presence of air and I_2 in benzene or methanolic solution. In the thiophene series, ester-acid **9**, diacid **11** and diester **13** photodehydrocyclized into the corresponding dehydro products of twofold photochemical dehydrocyclization reaction: dinaphtho[2,1–b:1',2'–d]thiophene–5,9–dimethoxylate (**26**), dinaphtho[2,1–b:1',2'–d]thiophene–5,9–dicarboxylic acid (**27**) and 9–carbomethoxy–dinaphtho[2,1–b:1',2'–d]thiophene–5–carboxylic acid (**28**). The best yields (over 50%) were obtained on **26** when **13** was irradiated in benzene solution. The same compound was prepared by onefold photochemical dehydrocyclization reaction from **29** (see Scheme 4).



Sheme 4.

Diacid **27** was obtained in 4% yield by irradiating methanolic solution of **11** (see Scheme 1). The same compound was obtained in better yields by hydrolysis of **26** (see Scheme 5).



Sheme 5.

Acid-ester **28** was obtained in 2% yield by irradiating methanolic solution of **9**. The same compound was prepared by onefold photochemical dehydrocyclization reaction from **23** (over 12% yield). In the furan series, only dimethyl dinaphtho[2,1–b:1',2'–d]furan–5,9–dimethoxylate (**30**) was prepared from distyryl derivative **14** by twofold photochemical dehydrocyclization reaction in a very low yield. Distyrylfuran compound **10** was not photochemically cyclized into 9–carbomethoxydinaphtho[2,1–b:1',2'–d]furan–5–carboxylic acid (**31**) but **31** was prepared by onefold photochemical dehydrocyclization reaction from **24**. Dinaphtho[2,1–b:1',2'–d]furan–5.9–dicarboxylic acid (**32**) was not photochemically prepared from distyrylfuran derivative **12**, but by hydrolysis of **30**. Yields in the photochemical reactions in the thiophene series were higher than in the furan series, where a lot of resins were left over.

The mechanism of the twofold photochemical reaction was examined. The twofold photochemical dehydrocyclization reaction in the benzene series suggests that the reaction proceeds in two steps over styrylphenanthrene as intermediate.[8,9] We tried to investigate whether the reaction was proceeding according to the literature, namely »step by step« over styrylnaphtho[2,1–b]thiophene derivative (**29**) as the product of the first onefold photochemical dehydrocyclization reaction starting from **13** or in one step. It was one of the reasons why we synthesized **29** and **24**. Irradiation experiments were performed so that after different irradiation times the aliquots of the reaction mixture were taken out and detected by GC. In no interval of time was it possible to detect the presence of **29**. After 4 hours of irradiation, **26** was present in the reaction mixture together with **13** while after 24 hours of irradiation the reaction mixture consisted predominantly of **26**, a little **13** was still present but **29** did not appear.

Measuring the rates of the photochemical conversion of **13** into **26** and **29** into **26** by irradiation of the benzene solutions (5 mg in 5 ml of solvent with a 400 W lamp taking aliquots during 4 hours) and detecting the changes of the extinction coefficients of **13** and **29** in UV spectroscopy, we deduced that the rate of photochemical transformation of **29** into **26** was more rapid than the rate of photochemical transformation of **13** into **26**. For this reason, we were not able to conclude if the reaction proceeded directly from **13** into **26** or in two steps, namely **13** → **29** → **26**.

EXPERIMENTAL

M.ps. are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer in KBr discs. UV spectra were taken on a Perkin-Elmer 124 spectrophotometer using methanolic solution. ^{1}H NMR spectra were recorded on Jeol J.M.M. FX 100 FT spectrometer with TMS as internal standard in $CDCl_3$ or DMSO–d_6. Irradiation was performed by water cooled immersion well equipped with an »Original Hanau« 125 W high pressure mercury arc lamp using pyrex filter or inside a »Rayonet« photochemical reactor provided with 300 or 254 nm lamps. Gas chromatography was conducted on a Pye Unicam 4550 apparatus equipped with capillary column CPSi18CB 25 m at 300 °C and a stream of hydrogen of 3 ml/min.

*3–(2–Thienyl)–2–phenylacrylic Acids (**1**) and (**2**)*[1,2]

Phenylacetic acid (13.6 g, 0.1 mol) and 2–thiophenecarboxaldehyde (13.4 g, 0.12 mol) in a mixture of triethylamine (20 ml) and acetic acid anhydride (20 ml) were refluxed for 3 hours. After the reaction was completed, the mixture was cooled, acidified with hydrochloric acid and extracted with ether. The organic layer was washed with water and the acid was extracted into 10% sodium carbonate solution. The alkaline solution of sodium salts was boiled with charcoal, filtered off and cooled, than acidified to pH 5 with acetic acid. The precipitated *E* isomer **1** was filtered off and recrystallized from methanol (yield 13.8 g, 60%), m.p. 186–188 °C (lit.[2] 186–188

°C). Hydrochloric acid was added to the filtrate and an additional crystalline crop consisting of the corresponding *Z* isomer was filtered off (1 g, 4%), m.p. 135–136 °C.

3–(2–Furyl)–2–phenylacrylic Acids (**3**) *and* (**4**)

Compounds **3** and **4** were prepared in a manner similar to the preparation of **1** and **2** by three hours heating of furfural (43 ml, 0.52 mol), phenylacetic acid (56.6 g, 0.42 mole), acetic acid anhydride (100 ml) and triethylamine (100 ml). After recrystallization from methanol *E* isomer (41.1 g, 49%) was obtained, m.p. 130–132 °C (lit.[3] m.p. 129–132 °C). Recrystallized (benzene:petrolether) white crystals of *Z* isomer (18.1 g, 21%) were obtained, m.p. 104–106 °C (lit.[3] m.p. 104–107 °C).

Methyl E–3–(2–thienyl)–2–phenylacrylate (**5**)[4]

Methyl ester **5** was prepared by five hours refluxing of **1** (25 g, 0.11 mole) dissolved in cca 500 ml of absolute methanol to which conc. sulfuric acid (5 ml) was added. The cooled reaction mixture was poured onto 500 g of crushed ice, crystallized ester was recrystallized from methanol (21.3 g, 85%), m.p. 79–81 °C (lit.[4] 79–81 °C).

Methyl E–3–(2–furyl)–2–phenylacrylate (**6**)[5]

Methyl ester **6** was prepared in a manner similar to the preparation of **5**, by three hours heating of 3 (10 g, 46.7 mmole) dissolved in absolute methanol (150 ml) to which conc. sulfuric acid (1.5 ml) was added. Recrystallized product (methanol:water) (8.6 g, 80%) was obtained, m.p. 77–78 °C.

Methyl E–3–(5–formyl–2–thienyl)–2–phenylacrylate (**7**)[10]

Methyl ester **5** was formylated by Vilsmeier formylation. Phosphorous oxychloride (35 g, 0.21 mole) was added dropwise with cooling to *N,N*–dimethylformamide (15.3 g, 0.21 mole). The mixture was stirred for half–an-hour by cooling on ice, the apparatus being protected with a calcium chloride tube. A solution of **5** (21 g, 86 mmole) in DMF (10 ml) was added dropwise to the mixture. After the addition was completed, the mixture was stirred for an hour at room temperature, then heated at 90 °C for three hours, cooled and poured onto crushed ice (400 g) and made weakly alkaline with sodium carbonate solution, and left overnight on ice. The solid was filtered off, washed with water and recrystallized from methanol. White crystals (20.3 g, 87%) were obtained, m.p. 120–121 °C.

Methyl E–3–(5–formyl–2–furyl)–2–phenylacrylate (**8**)

The corresponding methyl ester **6** (13 g, 57 mmole) was formylated in a manner similar to the preparation of **7** with $POCl_3$ (22.8 ml, 0.25 mole) and DMF (20 ml, 0.25 mole). The product was recrystallized from methanol. Orange crystals (12.2 g, 83.5%) were obtained, m.p. 103–105 °C; IR (cm^{-1}): 1710($COOCH_3$), 1665(CHO), 1630(C=C); ^1H NMR (acetone–d_6, δ/ppm): 9.57 (s, 1H, CHO), 7.65 (s, 1H, ethylenic), 7.50–7.17 (m, 5H, arom.), 7.00 (d, 1H, $J_{3,4}$ = 3.51 Hz,H–4), 5.76 (d, 1H, $J_{3,4}$ = 3.51 Hz, H–3), 3.80 (s, 3H, OCH_3).

Anal. Calcd for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72;

Found: C, 70.12; H, 4.59.

E–2–(2–Carboxystyryl)–E–5–(2–carbomethoxystyryl)thiophene (**9**)

Compound **9** was prepared from **7** (6 g, 22 mmole), phenylacetic acid (2,5 g, 18 mmole), triethylamine (4 ml) and acetic acid anhydride (4 ml) by 1.5 hours refluxing in a manner similar to the preparation of **1** and **2**. After recrystallization, yellow crystals (2.3 g, 27%) were obtained, m.p. 217–219 °C; IR (cm^{-1}): 1705($COOCH_3$), 1665(COOH), 1610(C=C), 1595(C=C); ^1H NMR (DMSO–d_6, δ/ppm): 7.85 (s, 1H, ethylenic), 7.82 (s, 1H, ethylenic), 7.43–7.27 (m, 8H, six arom. + two thiophenic), 7.00–6.92 (m, 4H, arom.), 3.63 (s, 3H, OCH_3).

Anal. Calcd for $C_{23}H_{18}O_4S$: C, 70.75; H, 4.65;

Found: C, 70.90; H, 4.46.

E–2–(2–Carboxystyryl)–E–5–(2–carbomethoxystyryl)furan (**10**)

This compound was prepared from **8** (1.8 g, 7 mmole) and phenylacetic acid (0.82 g, 6 mmole) in triethylamine (10 ml) and acetic acid anhydride (10 ml) by three hours refluxing in a manner similar to the preparation of **9**. Yellow crystals of *E,E*–isomer (1.6 g, 61%) were obtained, m.p. 162–167 °C; IR (cm^{-1}): 1710($COOCH_3$), 1680(COOH), 1610(C=C); ^1H NMR (acetone-d_6, δ/ppm): 7.46–7.18 (m, 12H, arom.+ethylenic), 5.69 (s, 2H, furanic), 3.71 (s, 3H, OCH_3).

Anal. Calcd for $C_{23}H_{18}O_5$: C,73.79; H, 4.85;

Found: C, 73.55; H, 4.62.

E,E–2,5–Di–(2–carboxystyryl)thiophene (**11**)

Diacid **11** was prepared by hydrolysis of **9** (3.32 g, 8.5 mmole), which was added to the solution of sodium hydroxide (0.52 g, 13 mmole) in water:methanol (4 ml:50 ml) and refluxed for 1.5 hours. Methanol was distilled off in vacuo, the residue dissolved in water, acidified with conc. hydrochloric acid and a crude product recrystallized from methanol. Yellow crystals (2.9 g, 90%) were obtained, m.p. 310–312 °C; IR (cm^{-1}): 1670 (COOH), 1608 (C=C), 1592 (C=C); ^1H NMR (DMSO-d_6, δ/ppm): 7.77 (s, 2H, ethylenic), 7.41–7.18 (m, 8H, arom.+two thiophenic), 7.01–6.91 (m, 4H, arom).

Anal. Calcd for $C_{22}H_{16}O_4S$: C, 70.20; H, 4.28;

Found: C, 70.30; H, 3.98.

E,E–2,5–Di–(2–carboxystyryl)furan (**12**)

Diacid **12** was prepared by hydrolysis of **10** (3.3 g, 8.5 mmole) in a manner similar to the preparation of **11**. Yellow powder (2.9 g, 97%) was obtained, m.p. 248–249 °C; IR (cm^{-1}): 1660 (COOH), 1610 (C=C); ^1H NMR (acetone-d_6, δ/ppm): 7.48–7.20 (m, 12H, arom.+ethylenic), 5.72 (s, 2H, furanic).

Anal. Calcd for $C_{22}H_{16}O_5$: C, 73.32; H, 4.48;

Found: C, 73.28; H, 4.23.

E,E–2,5–Di–(2–carbomethoxystyryl)thiophene (**13**)

Diester **13** was prepared from **9** (1.5 g. 4 mmole) dissolved in absolute methanol (200 ml) and conc. sulfuric acid (2 ml) was added. The reaction mixture was refluxed for 7 hours, methanol was distilled off to half of the volume, the reaction mixture was cooled and poured onto crushed ice. The precipitate was filtered off. Yellow crystals (1.45 g, 90%) were obtained, m.p. 128–129 °C; IR (cm^{-1}): 1700($COOCH_3$), 1610(C=C), 1600(C=C); ^1H NMR (DMSO-d_6, δ/ppm); 7.85 (s, 2H, ethylenic), 7.45–7.17 (m, 8H, six arom.+two thiophenic), 7.01–6.91 (m, 4H, arom.), 3.63 (s, 6H, OCH_3).

Anal. Calcd for $C_{24}H_{20}O_4S$: C, 71.27; H, 4.98;

Found: C, 71.03; H, 5.07.

E,E–2,5–Di–(2–carbomethoxystyryl)furan (**14**)

Diester **14** was prepared from **10** (0.5 g, 1.34 mmole in 50 ml of methanol + 0.5 ml conc. sulfuric acid) in a manner similar to the preparation of **13**. The product was recrystallized from methanol. Yellow crystals (0.4 g, 77%) were obtained, m.p. 114–115 °C; IR (cm^{-1}): 1700($COOCH_3$), 1610(C=C); ^1H NMR (acetone-d_6, δ/ppm): 7.47–7.17 (m, 12H, arom.+ethylenic), 5.68 (s, 2H, furanic), 3.71 (s, 6H, OCH_3).

Anal. Calcd for $C_{24}H_{20}O_5$: C, 74.21; H, 5.19;

Found: C, 74.32; H, 5.27.

Naphtho[2,1–b]thiophene–5–carboxylic Acid (**15**)[2]

Compound **1** (1.5 g, 6.5 mmole) was dissolved in cyclohexane (2 l), I_2 (0.1 g) was added and the mixture was irradiated for 8 days. The air was bubbled through the solution. The precipitated

crystals were filtered off and recrystallized from methanol. White crystals (0.7 g, 47%) were obtained, m.p. 270–271 °C. (Lit.[2] 267–268 °C).

Naphtho[2,1-b]furan-5-carboxylic Acid (**16**)[6]

This compound was prepared in the manner described for **15**. Compound **3** (4.24 g, 19.8 mmole) was dissolved in cyclohexane (2.5 l), I_2 (0.25 g) was added and the solution irradiated for 100 hours. The crystals were recrystallized from methanol. Light brown crystals (2.2 g, 58%), m.p. 234–235 °C (lit.[6] m.p. 234–235 °C) were obtained.

Methyl naphtho[2,1-b]thiophene-5-carboxylate (**17**)[3]

This compound was prepared from **5** (100 mg, 0.41 mmole, in 100 ml of cyclohexane) by 24 hours irradiation. The air was bubbled through the solution. Precipitated crystals were filtered off and recrystallized from methanol. Crystals (50 mg, 50%) were obtained, m.p. 94–95 °C. (Lit.[3] 94–95 °C).

Methyl naphtho[2,1-b]furan-5-carboxylate (**18**)

Freshly prepared etheral solution of CH_2N_2 (about 3 g in 200 ml of ether) was added to **16** (4 g, 18.9 mmole) in ether and allowed to stand overnight. Ether was evaporated and the brown oil was chromatographed on a column (silica gel) with chloroform:carbontetrachloride (1:1). Yellow crystals of **18** (2 g, 47%) were obtained, m.p. 48–50 °C; IR(cm^{-1}): 1720($COOCH_3$); ^1H NMR($CDCl_3$, δ/ppm): 9.13–8.98 (m, 1H, H–6), 8.43 (d, 1H, $J_{1,4}$ = 0.88 Hz, H–4), 8.23–8.11 (m, 1H, H–9), 7.87 (d, 1H, $J_{1,2}$ = 2.05 Hz, H–2), 7.66–7.55 (m, 2H, H–7 and H–8), 7.30–7.27 (dd, 1H, $J_{1,2}$ = 2.05 Hz, $J_{1,4}$ = 0.88 Hz, H–1), 4.02 (s, 3H, OCH_3).

Anal. Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46;

Found: C, 74.28; H, 4.35.

All attempts to prepare **18** photochemically from **6** gave no result. Compound **6** got decomposed.

Methyl 2-formylnaphtho[2,1-b]thiophene-5-carboxylate (**19**)[10]

A solution of ester-aldehyde **7** (100 mg, 0.37 mmole) in cyclohexane (100 ml) and in the presence of I_2 traces was irradiated by pyrex filtered light for 10 hours at room temperature. Air was bubbled through the solution. During irradiation, a pale yellow deposit was formed which was filtered off and recrystallized from benzene:hexane. White crystals (60 mg, 60%) were obtained, m.p. 181–182 °C. (Lit.[10] 183–185 °C).

Methyl 2-formylnaphtho[2,1-b]furan-5-carboxylate (**20**)

N-methylformanilide (0.21 ml, 2.4 mmole) was cooled on ice and $POCl_3$ (0.22 ml, 2.4 mmole) was added by stirring. The mixture was stirred at room temperature for 15 minutes. 1,2-Dichloroethane (0.6 ml) was added to the mixture and the solution was cooled on ice. Then, a solution of **18** (0.3 g, 1.33 mmol) in 1,2-dichloroethane (0.6 ml) as added dropwise. When all of the solution was added, the mixture was stirred on ice for 0.5 hours and at room temperature for 0.5 hours, then it was refluxed for 5 hours. After that, the mixture was cooled and poured on crushed ice and neutralized with 10% solution of sodium carbonate and left on ice overnight. The reaction mixture was then extracted with ether. The organic layer was dried over anhydrous sodium sulfate and evaporated in *vacuo*. The oily residue was chromatographed on a column (silica gel) using chloroform:carbontetrachloride (1:1) as eluent. The crystals were recrystallized from methanol (0.13 g, 39%), m.p. 89–90 °C; IR(cm^{-1}): 1710($COOCH_3$), 1680(CHO); ^1H NMR($CDCl_3$, δ/ppm): 9.96 (s, 1H, CHO), 9.05–8.93 (m, 1H, H–6), 8.35 (d, 1H, $J_{1,4}$ = 0.88 Hz, H–4), 8.26–8.12 (m, 1H, H–9), 8.01 (d, 1H, $J_{1,4}$ = 0.88 Hz, H–1), 7.74–7.63 (m, 2H, H–7 and H–8), 4.05 (s, 3H, OCH_3).

Anal. Calcd for $C_{15}H_{12}O_4$: C, 70.31; H, 4.72;

Found: C, 70.35; H, 4.72.

All attempts to prepare **20** photochemically from **8** gave no result.

E–3–(5–Formyl–2–furyl)–2–phenylacrylic Acid (**21**)

This compound was prepared from **8** (11 g, 43 mmole) to which sodium hydroxide solution (2.6 g, 65 mmole) in methanol:water mixture (250:20 ml) was added in a manner similar to the preparation of **11**. Yellow crystals (8.9 g, 85%) were obtained, m.p. 255–257 °C; IR(cm^{-1}): 1690(COOH), 1665(CHO), 1620(C=C); ^{1}H NMR ($CDCl_3$, δ/ppm): 9.55 (s, 1H, CHO), 7.81 (s, 1H, ethylenic). 7.50–7.24 (m, 5H, arom.), 7.00 (d, 1H, $J_{3,4}$=3.51 Hz, H–4), 5.83 (d, 1H, $J_{3,4}$=3.51 Hz, H–3).

Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16;

Found: C, 69.30; H, 4.38.

All attempts to prepare **22** photochemically from **21** gave no result. The compound **21** was decomposed.

Methyl E–2–(2–carboxystyryl)naphtho[2,1–b]thiophene–5–carboxylate (**23**)

This compound was prepared from **19** (1.5 g, 5.8 mmole), phenylacetic acid (0.68 g, 5.0 mmole), triethylamine (15 ml) and acetic acid anhydride (15 ml) by 1.5 hours refluxing in a manner similar to the preparation of **1** and **2**. The crude product was recrystallized from methanol. Yellow crystals (0.72 g, 31.9%), m.p. 221–222 °C were obtained.

IR(cm^{-1}): 1710($COOCH_3$), 1680(COOH), 1615(C=C), 1600(C=C); ^{1}H NMR (DMSO–d_6, δ/ppm): 8.83–8.68 (m, 1H, H–6), 8.64 (s, 1H, H–4), 8.55–8.43 (m, 1H, H–9), 8.42 (s, 1H), 8.22 (s, 1H), 7.74–7.66 (m, 2H, H–7, H–8), 7.57–7.46 (m, 3H, arom.), 7.36–7.29 (m, 2H, arom.), 3.90 (s, 3H, OCH_3).

Anal. Calcd for $C_{23}H_{16}O_4S$: C, 71.12; H, 4.15;

Found: C, 71.03; H, 4.34.

During isolation, when the alkaline extracts of **23** were heated with charcoal, filtered and acidified with acetic acid, **23** was partly hydrolyzed to **25**. **25** was isolated in traces m.p. 305–307 °C; IR(cm^{-1}): 1670(COOH); 1615(C=C); ^{1}H NMR (DMSO–d_6, δ/ppm): 8.95–8.88 (m, 1H, H–6), 8.66 (s, 1H, H–4), 8.52–8.42 (m, 1H, H–9), 8.41 (s, 1H), 8.24 (s, 1H), 7.74–7.30 (m, 7H, H–7 and H–8+5 arom.).

Anal. Calcd for $C_{22}H_{14}O_4S$: C, 70.58; H, 3.77;

Found: C, 70.79; H, 4.01.

Methyl E–2–(2–carboxystyryl)naphtho[2,1–b]furan–5–carboxylate (**24**)

Compound **24** was prepared from **20** (0.3 g, 1.18 mmole), phenylacetic acid (0.15 g, 1.1 mmole) in acetic anhydride (4 ml) and triethylamine (4 ml) in a manner similar to the preparation of **1** and **2**. Yellow crystals of *E* isomer (0.1 g, 23%) were obtained, m.p. 177–179 °C; IR(cm^{-1}): 1720($COOCH_3$), 1690(COOH), 1615(C=C); ^{1}H NMR (DMSO–d_6, δ/ppm): 8.99–8.77 (m, 1H, H—6), 8.46–8.36 (m, 1H, H–9), 8.29 (d, 1H, $J_{1,4}$=0.59 Hz, H–4), 8.01 (d, 1H, $J_{1,4}$=0.59 Hz, H–1), 7.78–7.24 (m, 8H, arom., H–7, H–8 and ethylenic), 3.98 (s, 3H, OCH_3).

Anal. Calcd for $C_{23}H_{16}O_5$, 74.18; H, 4.33;

Found: C, 74.25; H, 4.63.

Z isomer was present in traces.

Dinaphtho[2,1–b:1',2'–d]thiophene–5,9–dimethoxylate (**26**)

Compound **13** (50 mg, 0.12 mmole) was dissolved in benzene (100 ml), a few crops of I_2 (1.5 mg) were added and the solution was irradiated until the peak of the starting compound **13** disappeared in UV spectrum (about 60 hours). During irradiation, the air was bubbled through the solution. The precipitated crystals were filtered off, washed with the water solution of $NaHSO_3$, water and methanol. Yellow crystals (23.5 mg, 47%) were obtained, m.p. > 320 °C. When the reaction was carried out in methanol, the yield was only 11%; IR(cm^{-1}): 1710($COOCH_3$); ^{1}H NMR($CDCl_3$, δ/ppm): 9.09–8.78 (m, 4H, H–1, H–4, H–10 and H–13), 8.66 (s, 2H, H–6 and H–8), 7.70–7.54 (m, 4H, H–2, H–3, H–11 and H–12), 4.08 (s, 6H, OCH_3).

Anal. Calcd for $C_{24}H_{16}O_4S$: C, 72.00; H, 4.03;

Found: C, 72.24; H, 4.01.

Dinaphtho[2,1-b:1',2'-d]thiophene-5,9-dicarboxylic Acid (**27**)

Method A: Diacid **11** (100 mg, 0.27 mmole) was dissolved in methanol, a few crops of I_2 were added and the solution was irradiated for 7 hours through pyrex filtered light. The solvent was evaporated, the residue was washed with $NaHSO_3$ solution to remove I_2 and then with water. The residue was washed with few drops of methanol, where resins were dissolved and undissolved crystals were filtered off. Yellow crystals (4 mg, 4%) were obtained, m.p. > 320 °C.

Method B: Compound **26** (100 mg, 0.25 mmole) was hydrolyzed with a solution of sodium hydroxyde (0.5 g, NaOH, 2 ml H_2O and 20 ml of methanol) by 24 hours refluxing. Methanol was distilled off, and the residue dissolved in water and acidified with conc. hydrochloric acid. Pale yellow crystals (53 mg, 57%) were obtained. The crystals are very slightly soluble in organic solvents and the analytical sample was prepared by washing them in different solvents. IR(cm^{-1}): 1670(COOH); ^1H NMR(DMSO-d_6, δ/ppm): 9.04–8.69 (m, 4H, H–1, H–4, H–10 and H–13), 8.87 (s, 2H, H–6 and H–8), 7.78–7.65 (m, 4H, H–2, H–3, H–11 and H–12).

Anal. Calcd for $C_{22}H_{12}O_4S$: C, 70.97; H, 3.25;

Found: C, 70.84; H, 3.33.

9-Carbomethoxydinaphtho[2,1-b:1',2'-d]thiophene-5-carboxylic Acid (**28**)

Method A: This compound was prepared by pyrex filtered UV-irradiation of the methanolic solution (100 ml) of **23** (68 mg, 0.18 mmole) for 5 hours in a manner similar to preparation of **26**. Yellow crystals (8 mg, 12%) were obtained, m.p. >320 °C.

Method B: Compound **9** (50 mg, 0.13 mmole) was dissolved in methanol (100 ml) and irradiated for 4 hours in a manner similar to the preparation of **26**. The precipitates were filtered off. Yellow crystals (1 mg, 2%) were obtained. The crystals were very slightly soluble and the analytical sample was prepared by washing in different solvents: IR(cm^{-1}): 1715($COOCH_3$), 1695(COOH); ^1H NMR(unisol, δ/ppm): 9.05–8.75 (m, 4H, H–1, H–4, H–10 and H–13), 8.71 (s, 1H, H–6), 8.69 (s, 1H, H–8), 7.72–7.67 (m, 4H, H–2, H–3, H–11 and H–12), 4.07 (s, 3H, OCH_3).

Anal. Calcd for $C_{23}H_{14}O_4S$: C, 71.50; H, 3.65;

Found: C, 71.28; H, 3.70.

Methyl E-2-(2-carbomethoxystyryl)naphtho[2,1-b]thiophene-5-carboxylate (**29**)

Compound **29** was prepared in a manner similar to the preparation of **5** by dissolving **23** (60 mg, 0.16 mmole) in methanol (50 ml) to which conc. sulfutic acid (0.5 ml) was added. Yellow crystals (50 mg, 80%) were obtained, m.p. 206–208 °C; IR(cm^{-1}):1710($COOCH_3$), 1700 ($COOCH_3$), 1615(C=C), 1600(C=C); ^1H NMR($CDCl_3$, δ/ppm): 9.10–8.90 (m, 1H, H–6), 8.37 (s, 1H, H–4), 8.31–8.15 (m, 2H, H–9 and H–1 or ethylenic), 8.06 (s, 1H, H–1 or ethylenic), 7.70–7.40 (m, 7H, H–7, H–8 and arom.), 3.97 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3).

Anal. Calcd for $C_{24}H_{18}O_4S$: C, 71.62; H, 4.51;

Found: C, 71.38; H, 4.69.

Dinaphtho[2,1-b:1',2'-d]furan-5,9-dimethoxylate (**30**)

Diester **14** (0.5 g, 1.3 mmole) was dissolved in methanol (250 ml) and irradiated for 50 hours. A yellow crystalline deposit (15 mg, 3%) was collected, m.p. 250–251 °C; IR(cm^{-1}): 1725 ($COOCH_3$); ^1H NMR($CDCl_3$, δ/ppm): 9.20–9.03 (m, 4H, H–1, H–4, H–10 and H–13), 8.47 (s, 2H, H–6 and H–8), 7.80–7.63 (m, 4H, H–2, H–3, H–11 and H–12), 4.07 (s, 6H, OCH_3).

Anal. Calcd for $C_{24}H_{16}O_5$: C, 75.00; H, 4.20;

Found: C, 75.08; H, 4.09.

9-Carbomethoxydinaphtho[2,1-b:1',2'-d]furan-5-carboxylic Acid (**31**)

Compound **24** (11 mg, 0.03 mmole) was dissolved in methanol (100 ml) and irradiated for six hours. The solution was evaporated and a few drops of methanol were added to the residue. Undissolved crystals were filtered off. Yellow crystals (1.2 mg, 11%), m.p. 305–308 °C were ob-

tained. IR(cm^{-1}): 1720($COOCH_3$); 1700(COOH); ^1H NMR (unisol, δ/ppm): 9.16–9.10 (m, 4H, H–1, H–4, H–10 and H–13), 8.56 (s, 1H, H–6), 8.54 (s, 1H, H–8), 7.87–7.71 (m, 4H, H–2, H–3, H–11 and H–12), 4.08 (s, 3H, OCH_3).

Anal. Calcd for $C_{23}H_{14}O_5$: C, 74.59; H, 3.81;

Found: 74.39; H, 3.88.

All attempts to prepare **31** photochemically from **10** gave no result. Compound **10** was decomposed.

*Dinaphtho[2,1–b:1',2'–d]furan–5,9–dicarboxylic Acid (**32**)*

Diacid **32** was prepared by hydrolysis of diester **30** (25 mg, 0.065 mmole) with sodium hydroxide solution (100 mg NaOH, 2 ml H_2O, 20 ml methanol) in a manner similar to the preparation of **11**. Light yellow crystals (20 mg, 86%) were obtained, m.p. > 320 °C; IR(cm^{-1}): 1700(COOH); ^1H NMR(DMSO–d_6, δ/ppm): 9.17–9.00 (m, 4H, H–1, H–4, H–10 and H–13), 8.54 (s, 2H, H–6 and H–8), 8.00–7.75 (m, 4H, H–2, H–3, H–11 and H–12).

Anal. Calcd for $C_{22}H_{12}O_5$: C, 74.16; H, 3.39;

Found: C, 74.10; H, 3.41.

All attempts to prepare **32** by twofold photochemical dehydrocyclization reaction from **12** gave no result. Compound **12** was decomposed.

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SAŽETAK

Reakcija dvostruke fotokemijske dehidrociklizacije supstituiranih 2,5–distiriltiofena i 2,5–distirilfurana

Miroslav Bajić, Grace M. Karminski-Zamola i Nikola Blažević

Istraživana je fotokemija 2,5–distiriltiofena i 2,5–distirilfurana. Nastali derivati dinafto[2,1–b:1',2'–d]tiofena **26**, **27** i **28** i dinafto[2,1–b:1',2'–d]furana (**30**) detektirani su kao produkti reakcije dvostruke fotokemijske dehidrociklizacije. Derivat dinafto[2,1–b:1',2'–d]furana (**31**) priređen je reakcijom jednostruke fotokemijske dehidrociklizacije iz stiril–derivata nafto [2,1–b]furana **24**, dok je dinafto[2,1–b:1',2'–d]furanski derivat **32** priređen hidrolizom **30**. Nije zamijećeno nastajanje *E*–2–(2–karboksistiril)nafto[2,1–b]tiofen–5–metoksilata (**23**) ili *E*–2–(2–karboksistiril)nafto[2,1–b]furan–5–metoksilata (**24**) kao produkata reakcije jednostruke fotokemijske dehidrociklizacije polazeći od derivata 2,5–distiriltiofena **9** ili 2,5–distirilfurana **10**. Međutim ovi su sintetizirani iz **19** i **20** prema shemi. Mehanizam reakcije je kratko prodiskutiran.