



# Acid-induced dimerisation of 1,2-di(thien-2-yl)ethanone

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Received 20 February 2003; revised 10 March 2003; accepted 3 April 2003

**Abstract**—Treatment of 1,2-di(thien-2-yl)ethanone with aqueous 75% (v/v) sulfuric acid gives a dimer in which the units are linked head-to-head via a thiophene–tetrahydrothiophene bond. © 2003 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Thiophene undergoes polymerisation in the presence of acids to give inter alia the trimer **1**<sup>1,2</sup> but the mechanism of the reaction is still a matter of conjecture. The protonation of thiophene clearly produces the cation **2** which might be expected to react with thiophene at either C2 or C4 to give the intermediate dimeric species **3** or **4**. Either of these, by subsequent protonation and further reaction with thiophene, could in principle produce the trimer **1**. Although the formation of the intermediate **4** is commonly assumed no firm evidence has been adduced for this. We have now prepared a dimeric thiophene derivative **7** which bears a close relationship to the dimer **4** and so provides support for this being the intermediate in the formation of the trimer **1**.

## 2. Discussion

During an examination of the alkylation of thiophene by ketones<sup>3</sup> we treated the dithienylethanone **5** with aqueous 75% (v/v) sulfuric acid in the expectation that it would undergo self-condensation, possibly forming a macrocyclic system. However, the product proved to be a dimer, C<sub>20</sub>H<sub>16</sub>O<sub>2</sub>S<sub>4</sub>, of the starting material which we formulate as the thienyltetrahydrothiophene derivative **7** on the basis of its NMR signals.

The <sup>13</sup>C and DEPT-135 NMR spectra of the dimer established that of the 20 carbon atoms seven were quaternary, while 10 were present in methine and three in methylene groups. In order to elucidate the structure fully we acquired the HSQC, <sup>1</sup>H–<sup>1</sup>H COSY and HMBC 2D NMR spectra<sup>4</sup> the first of which enabled the assignment of the protons attached to specific carbon atoms (see Table 1). The <sup>1</sup>H–<sup>1</sup>H COSY spectrum showed the presence of several spin systems, three of which we ascribe to a 2,5-

disubstituted and two 2-substituted thiophenes. The first consisted of H1–H2–H3 with correlations between H1 and H2, H2 and H3. The systems H8–H9 and H18–H19–H20 were revealed in a similar manner (see Table 1). In addition to a singlet for H6, a further spin system encompassed H11 to H15, including an allylic coupling between H12 and H15. The next step, the assembly of the spin systems, was complicated by the large number of quaternary carbons. Fortunately, there were adequate long range correlations in the HMBC spectrum to complete the process unambiguously. HMBC correlations from the carbonyl carbon C5 to H3 and H6 lengthened the substructure to include C1 to C6. A further correlation from the quaternary carbon C7 to H6 and H8 securely placed C7 in a thiophene ring and so added a second such ring to the substructure. A correlation from C10 to H9 completed this second thiophene ring system, and further correlations from C10 to H11, H12 and H14 added the spin system H11 to H15. The position of the last of the quaternary carbons, C17, followed from its correlations to H18, H19 and H20. Finally the carbonyl carbon C16 showed correlations to H15 and H18, so completing the skeletal structure of the dimer.

We solved the remaining problem, the configuration about the double bond at C13–C15, by a selective NOE experiment. Irradiation at  $\delta_{\text{H}}$  7.00 ppm (H15) gave strong NOEs at  $\delta_{\text{H}}$  7.66 ppm (H18) and  $\delta_{\text{H}}$  3.30 and 3.06 ppm (H12 and 12'). To confirm that these were consistent with the (*Z*)-configuration we constructed molecular models of both the (*E*)- and the (*Z*)- isomers of **7** and carried out a conformational search on each to locate the arrangement with minimum energy. In the model for (*Z*)-**4** the distances between H15 and H12/12' were 2.56 and 2.96 Å, and the H15–H18 distance was 2.39 Å, all of which would be expected to give rise to strong NOEs. In contrast the corresponding distances in (*E*)-**4** were 3.89 and 3.96 Å, and 2.27 Å, while no NOE between H15 and H12/12' would be visible because of the intervening double bond.

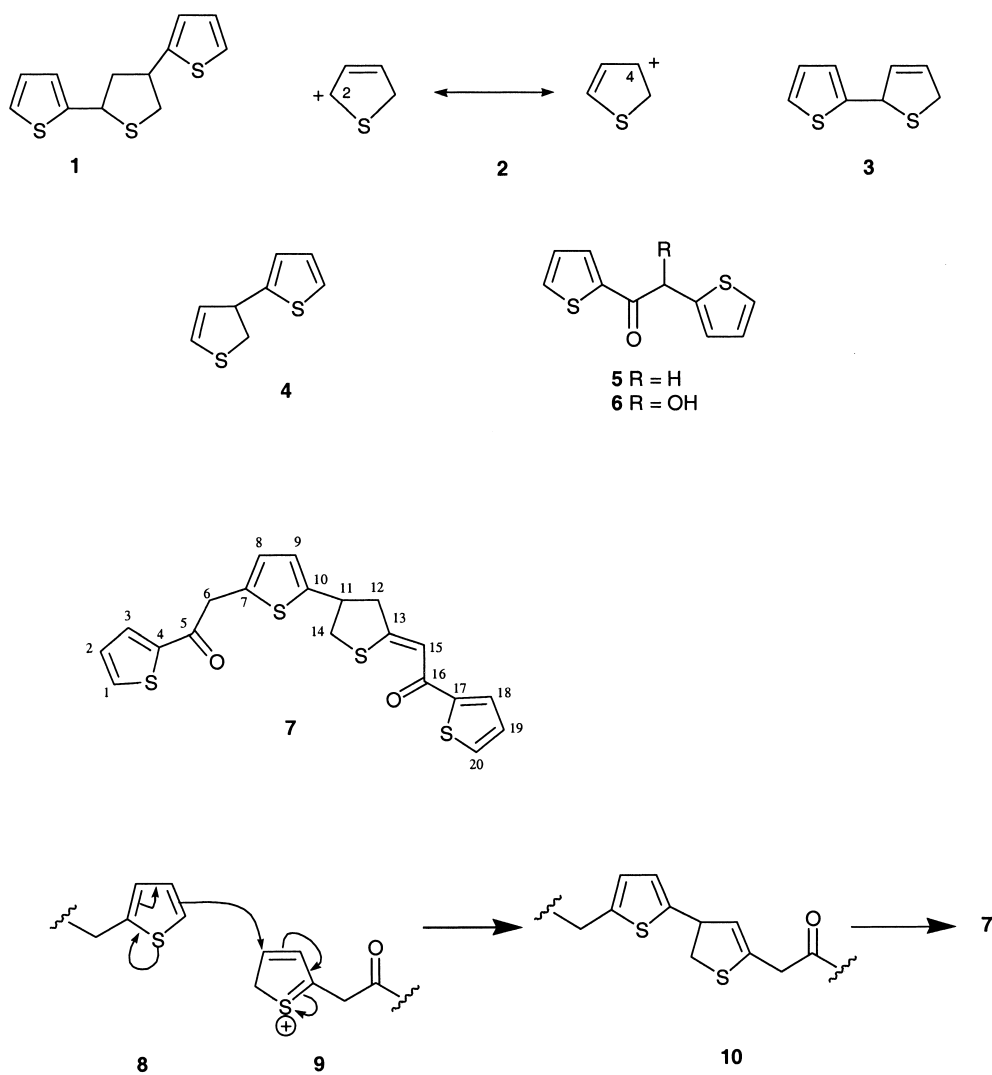
The UV absorption of the dimer shows a maximum at

**Keywords:** dimerisation; thiophene.

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**Table 1.**  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^1\text{H}$ - $^1\text{H}$  COSY and long range correlation data (HMBC,  $J=9$  Hz) for dimer **7** at 400/100 MHz in  $\text{CDCl}_3$ 

Atom	$\delta_{\text{C}}$ (ppm), mult.	$\delta_{\text{H}}$ (ppm), mult. ( $J$ in Hz)	COSY (H to H)	HMBC (C to H)
1	134.7, d	7.64, dd, 4.8, 1.2	2	2, 3
2	128.4, d	7.11, dd, 5.0, 4.0	1, 3	1, 3
3	132.9, d	7.76, dd, 4.0, 1.2	2	1, 2
4	143.2, s	–		1, 2, 3
5	189.0, s	–		3, 6
6	40.5, t	4.30, s	8	8
7	133.8, s	–		6, 8
8	126.9, d	6.76, s	6	6, 9
9	124.3, d	6.75, s		8, 11
10	144.0, s	–		9, 11, 12, 14
11	42.0, d	3.72, dddd, 10.4, 8.8, 6.4, 6.4	12, 14	9, 12, 14
12	47.3, t	3.30, dd, 16.0, 6.4, 3.06, ddd, 16.0, 10.4, 1.6	11, 15	14, 15
13	168.2, s	–		12, 14, 15
14	41.8, t	3.39, dd, 11.4, 6.4, 3.19, dd, 11.4, 8.8	11	12
15	111.4, d	7.00, broad t	12	12
16	181.1, s	–		15, 18
17	145.6, s	–		18, 19, 20
18	130.3, d	7.66, dd, 4.0, 1.2	19	19, 20
19	128.2, d	7.08, dd, 4.8, 4.0	18, 20	18, 20
20	132.7, d	7.54, dd, 4.8, 1.2	19	18, 19

**Scheme 1.**

significantly longer wavelength (344 nm) than that (at 283 nm) found<sup>5</sup> for the simple thenoyl system in 2-acetylthiophene. This is consistent with the presence in the dimer of an extended conjugated system such as that shown in structure 7.

The process of dimerisation would appear to involve the sequence shown in the Scheme 1, the thienyl group of one molecule 8 reacting initially with the protonated thienyl group 9 of another to give the thienyldihydrothiophene 10. In the presence of acid the latter then isomerises so that the olefinic bond moves into conjugation with the carbonyl group as in 7 so preventing further reaction. An unexpected feature of the initial dimerisation step is that the protonated thienyl group appears to be a better electrophile than does the protonated thenoyl group.

### 3. Experimental

#### 3.1. General

NMR spectra were recorded with a 400 MHz Varian Unity INOVA at 26°C in CDCl<sub>3</sub> using residual CHCl<sub>3</sub> as internal reference at 7.27 ppm. IR spectra were recorded for KBr discs or liquid films and UV absorption spectra for methanolic solutions. Mass spectra were obtained using electron impact at 70 eV. PLC was performed using Merck Kieselgel GF<sub>254</sub>. Molecular modelling<sup>6</sup> was carried out using MacroModel version 6.5. The (*E*) and (*Z*) isomers of 7 were constructed and subjected to 500 steps of minimisation with the MM2 forcefield using a continuum representation of the solvent, CHCl<sub>3</sub>. A Metropolis Monte-Carlo conformational search was conducted on each isomer to determine the preferred conformation (1000 steps). In each case the minimum energy conformation was encountered >100 times indicating that the most stable arrangement had indeed been located accurately.

**3.1.1. 1,2-Di(thien-2-yl)ethanone 5.** A mixture of thenoin<sup>7</sup> 6 (10.0 g, 44.6 mmol), powdered tin (9.45 g, 79.6 mmol) concentrated hydrochloric acid (9.5 ml) and ethanol (12.5 ml) was boiled under reflux for 24 h and filtered hot. Extraction of the filtrate with chloroform gave the

dithienylethanone 5 as a pale orange oil (5.2 g, 2.50 mmol, 56%) bp 140°C/0.5 mmHg (Found: M<sup>+</sup>, 208.0024. Calcd for C<sub>10</sub>H<sub>8</sub>OS<sub>2</sub>: M, 208.0016); *m/z* 208 (3%, M<sup>+</sup>), 111 (100, C<sub>4</sub>H<sub>3</sub>SCO), 97 (18, C<sub>4</sub>H<sub>3</sub>SCH<sub>2</sub>), 83 (7, C<sub>4</sub>H<sub>3</sub>S) and 45 (10, CHS); λ<sub>max</sub>/nm 243 (log ε 3.97), 259 (3.98) and 285.5 (3.89); ν<sub>max</sub>/cm<sup>-1</sup> 1660 (C=O); δ<sub>H</sub> (220 MHz, CDCl<sub>3</sub>) 4.39 (2H, s, CH<sub>2</sub>), 6.91–6.99 (2H, m, thienyl H3 and H5), 7.09–7.15 (1H, m, thienyl H4), 7.19 (1H, dd, *J*=4, 5 Hz, thenoyl H4), 7.64 (1H, d, *J*=5 Hz, thenoyl H3) and 7.76–7.80 (1H, d, *J*=4 Hz, thenoyl H5).

**3.1.2. Dimerisation of 1,2-di(thien-2-yl)ethanone.** A mixture of the dithienylethanone 5 (2.0 g, 9.61 mmol) and aqueous 75% (v/v) sulfuric acid (50 ml) was stirred at 20°C for 24 h, poured into water and extracted with chloroform. The product after PLC (chloroform) crystallised from chloroform-light petroleum (bp 60–80°C) to give (*Z*)-2-(2-thenoylmethylidene)-4-[5-(2-thenoylmethyl)thien-2-yl]tetrahydrothiophene 7 (385 mg, 0.93 mmol, 19.3%), mp 125–126°C (Found: M<sup>+</sup>, 416.0026. C<sub>20</sub>H<sub>16</sub>O<sub>2</sub>S<sub>4</sub> requires M, 416.0032); *m/z* 416 (15%, M<sup>+</sup>), 305 (10, M–C<sub>4</sub>H<sub>3</sub>SCO), 291 (4, M–C<sub>4</sub>H<sub>3</sub>SCOCH<sub>2</sub>) and 111 (100, C<sub>4</sub>H<sub>3</sub>SCO); λ<sub>max</sub>/nm 257 (log ε 4.20), 285infl (4.12) and 344 (4.35); ν<sub>max</sub>/cm<sup>-1</sup> 1654 (conj. C=O) and 1599 (aromatic C=C).

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