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Cyclopenta-thiophenes

IV.[1] Synthesis and Tautomeric Properties of 5-Nitro-4H- and 6H-Cyclopenta[b]thiophenes

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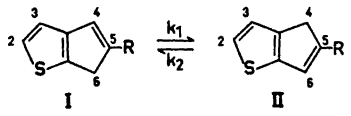
The synthesis of the two b-annelated thiophene isosters of 2-nitroindene is described. It is shown that they undergo fast tautomerism in the absence of added base. The position of the equilibrium is determined by NMR. The NMR spectra are discussed in some detail and the importance of certain specific long-range couplings is pointed out.

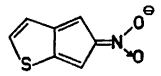
The only monosubstituted, b-annelated thiophene isosters of indene, reported to date, seem to be the methyl derivatives, 5-methyl-6H- and 4H-cyclopenta[b]thiophenes, I and II, R = CH_3.[2] Meth-Cohn and Gronowitz made some preliminary studies of the rate of equilibration of I, R = CH_3, with triethylamine as base.[2] They found that the rate was about ten times the rate of the corresponding tautomerism in the indene derivatives, and that the equilibrium mixture consisted of 76 % of II, R = CH_3 (at 32°C in deuterochloroform). Furthermore, no deuterium was incorporated when the reaction was carried out in deuteroethanol or in 10 % deuterium oxide in pyridine. These observations were taken as evidence for intramolecular prototropy.



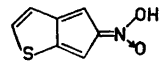
As part of a general study of cyclopenta-thiophenes, the present author wishes to report the synthesis and tautomeric properties of the 5-nitro-isomers, I and II, R = NO_2.

The purpose of changing the methyl group for a nitro group was to determine whether or not the energy difference defining the equilibrium was changed. No great change was expected since the position of the double bond

should primarily be influenced by the thiophene ring, and not by the substituent in the 5-position. Furthermore, it was of interest to study the rate of equilibration and make a comparison with the corresponding rate for I and II, R = CH_3. One should thereby obtain information about the importance of resonance structures such as III as contributors to the anion part of the ion-pair. More speculative, but not the least interesting, was the idea that it might be possible to demonstrate the existence of a third tautomer, resulting from *O*-protonation of III, *i.e.* the nitronic acid IV. Alternatively, derivatives of this very interesting tautomer might be obtainable.



III



IV

SYNTHESIS

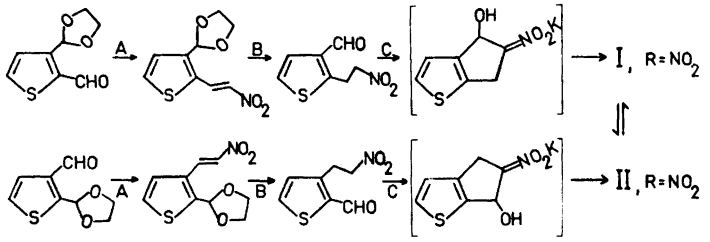
The synthesis of 2-nitroindene, of which I and II, R = NO_2, are isosters, starts with commercially available indene, which is reacted with nitrous acid and the resulting indene nitrite treated with steam;[3] or through reaction of indene with dinitrogen tetroxide and water followed by acetylation of the resulting nitro alcohol and subsequent elimination of acetic acid catalyzed by base.[4] Similar procedures for the synthesis of I and II, R = NO_2, were abandoned for two reasons: 1. The necessity of heat/base in the last steps would probably cause tautomerisms. 2. The starting materials needed, 6H-cyclopenta[b]thiophene and 4H-cyclopenta[b]thiophene, I and II, R = H, were not known; and even if they were synthesized, some doubt existed as to their stability in the above mentioned reactions.

Another route to 2-nitroindene involved sodium borohydride reduction of 3-hydroxy-2-nitroindene (obtainable from phthalaldehyde and nitromethane), and subsequent treatment with strong acid.[5] This procedure seemed worthwhile trying in the thiophene series. However, the condensation product from the reaction between 2,3-diformylthiophene and nitromethane consisted of two isomers,[1] the separation of which proved difficult, and, furthermore, an attempted sodium borohydride reduction resulted in tars only.

Therefore another approach was taken, which is outlined in the scheme. The key steps are base catalyzed cyclizations of 2-(β-nitroethyl)-3-thiophene aldehyde and 3-(β-nitroethyl)-2-thiophenealdehyde. The starting materials, 2-formyl-3-thiophenealdehyde ethylene acetal and 3-formyl-2-thiophenealdehyde ethylene acetal, were prepared according to known methods, the former from 3-thiophenealdehyde ethylene acetal by treatment with butyllithium followed by *N*,*N*-dimethylformamide,[6] and the latter from 3-bromo-2-thiophenealdehyde ethylene acetal by a similar procedure.[7]

The base catalyzed condensation of aromatic aldehydes with nitroalkanes is well known.[8] Its application to thiophene aldehydes[9] and thiophene dialdehyde [1] has been reported. The reactions of the two starting materials with nitromethane (A in the scheme) were conducted at 0 – 5°C in methanol solution with potassium hydroxide as base. When the reaction mixtures were treated

with concentrated hydrochloric acid and ice, the two β-nitrovinyl compounds were formed. As expected, partial hydrolyses of the acetal groups had occurred. As the protective groups were necessary even in the next steps (B in the scheme), the crude reaction products were refluxed with ethylene glycol in benzene solution with *p*-toluene sulfonic acid as catalyst, the water of reaction being removed azeotropically. The next steps (B) involved selective reduction of the carbon-carbon double bonds. Two methods were considered to achieve this: reduction with sodium borohydride and catalytic hydrogenation with tris(triphenylphosphine)rhodium chloride. Both methods have given satisfactory



Reaction sequences leading to 5-nitro-6H-, and 4H-cyclopenta[b]thiophene (I and II, $R=NO_2$).

Reactions:

(A)	1. $CH_3NO_2/KOH/CH_3OH$	2. HCl/H_2O	3. $HOCH_2CH_2OH/H^+/C_6H_6$
(B)	1. $NaBH_4/C_2H_5OH$	2. $AcOH/H_2O$	3. HCl/H_2O
(C)	1. KOH/CH_3OH	2. HCl/H_2O	

results in reductions of this type.[5, 10, 11] The first was chosen in this case, in view of its superiority with respect to yields and ease of operation, but even the other gave acceptable results.

The reductions were conducted by adding the substrate dissolved in ethanol to an ethanolic solution of sodium borohydride, thus maintaining a low concentration of unreacted substrate. In this way the undesired Michael addition of the nitronate to the β-nitrovinyl compound was minimized.

When the reductions were complete, the initially formed nitronates were converted to the nitro compounds by the action of acetic acid. Subsequent treatment with hydrochloric acid effected hydrolysis of the acetal groups. A direct treatment of the reaction mixture with strong acid would probably have resulted in Nef reactions,[1] with formation of the corresponding aldehydes. Yields in these reductions steps were 80 – 90 %.

The final steps (C) were intramolecular variants of the aldehyde-nitroalkane condensation, giving the desired products *via* the β-hydroxy nitronates (not isolated) depicted in the scheme. In this reaction, as well as in reactions A it is essential to use strong acid on the intermediate β-hydroxy nitronates to effect the formation of the β-nitrovinyl compounds. With weak acids, *e.g.* acetic acid, the corresponding saturated nitro alcohols are obtained. These are, contrary to a statement often made (repeated in a very recent book on nitro group chemistry [8]), most probably not intermediates in the formation of the

β-nitrovinyl compounds. This hypothesis is based on the observation that α-aryl-β-nitro alcohols do not undergo dehydrations under conditions prevailing in the arylaldehyde-nitromethane condensation as carried out in this work. In this connection the present author has suggested a mechanistic explanation for the ease with which these β-hydroxy nitronates are converted by strong acids to β-nitrovinyl aromatics.[1]

Before turning to a discussion of the title compounds, it may be in order to mention briefly another pathway to II, R = NO_2, which gave a rather unexpected result. Starting with 3-thiophenealdehyde, *via* the condensation product with nitromethane, 3-(β-nitroethyl)-thiophene was prepared by reduction with sodium borohydride. Now the introduction of an aldehyde group in the 2-position would give the same key intermediate as described above. The Vilsmeier-Haack formylation was attempted. Surprisingly, this method converted the primary nitro compound to the nitrile in high yield,[12] and thus this pathway was not further investigated.

DISCUSSION OF THE NMR SPECTRA

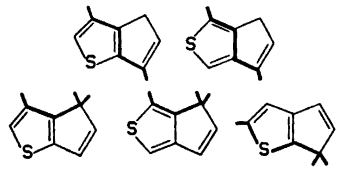
In contrast to the indenes,[13] the 4H-, and 6H-cyclopentathiophenes possess bands in the aromatic region of their NMR spectra of great simplicity. Furthermore, these bands may show specific long-range couplings which make unambiguous assignments possible.

One type of long-range coupling is confined to the 4H-systems and is a coupling over 5 bonds in an extended *planar* zig-zag configuration (all *trans*), illustrated in the first two formulas below. This coupling, which is of the magnitude 0.5 – 1.0 Hz, has been observed in many similar systems, including indene itself.[13,14] In II, R = CH_3[2] and R = NO_2, this coupling is not fully resolved, but nevertheless clearly visible as a broadening of the bands due to the 3- and 6-hydrogens. In 4-hydroxy-5-nitro-4H-cyclopenta[b]thiophene[1] and in 4H-cyclopenta[c]thiophene[15] this coupling has values of 0.8 and 0.7 Hz, respectively.

The other long-range couplings from the aromatic hydrogens are of the *ortho-* and *para*-benzylic types,[16] illustrated in the last three formulas below. Even these types of couplings may be of the magnitude 0.5 – 1.0 Hz, although they appear to be more influenced by structural factors than the first one.[1] In 4H-cyclopenta[c]thiophene the *ortho*-benzylic coupling, J_{34}, is as large as 1.4 Hz.[15] In II, R = CH_3[2] and R = NO_2, this coupling is not resolved. In I, R = NO_2, the *para*-benzylic coupling is seen as a broadening of the low-field aromatic doublet, which is consequently assigned to the 2-hydrogen. In this connection one may question the assignment made regarding the aromatic region in the spectrum of I, R = CH_3.[2] Here a well resolved triplet (J = 0.7 Hz) in the low-field part of the AB quartet is clearly distinguishable. This is most probably the result of a *para*-benzylic coupling (*vide supra*), and hence the low-field doublet is due to the 2-hydrogen even in this case.

Having thus assigned the aromatic bands in I and II, R = NO_2, the assignments of the other bands need no comments (see Experimental). J_{23} = 5.0 and 4.9 Hz, respectively, are quite normal for 2,3-disubstituted thiophenes,[17]

and also the allylic coupling constants, $J_{46} = 2.0$ and 1.9 Hz, are of the expected magnitudes.[18]



TAUTOMERIC PROPERTIES

The NMR spectrum of I, R = NO_2, was complicated by the rapid appearance of bands due to II, R = NO_2. In fact, this tautomeric conversion was so fast in deuterochloroform that it proved impossible to obtain the spectrum of pure I. The time taken from dissolving the compound until a reliable spectrum could be recorded (2 – 3 min) was sufficient for about 30 % of I to be converted to II. And after approximately 50 min (at 34°C) equilibrium values of 30 % I and 70 % II had been reached. That this was actually the thermodynamic equilibrium was shown by the following experiment. When II, R = NO_2, was kept in deuterochloroform solution for some hours, bands in its NMR spectrum ascribable to I, R = NO_2, appeared. After 2 – 3 days (at 34°C) a steady state had been reached, with the same composition as above.

Quantitative experiments were performed in which the rate of disappearance of I, R = NO_2, and the simultaneous formation of II, R = NO_2, were followed by integration of the respective CH_2-bands in the NMR spectra. The result of one of these experiments is recorded as a first-order plot in the diagram below. The temperature was 34°C and the solvent deuterochloroform. As seen from the graph, the kinetic data satisfy fairly well an equation for a reversible first-order reaction of the following type: $\ln(AK - B) = -(k_1 + k_2)t + \ln(A_0K - B_0)$ in which K is the equilibrium constant (~ 2.3) and A and B are the concentrations of I and II, respectively. From the slope of the straight line and the equilibrium constant, k_1 and k_2 may be calculated. However, when a similar experiment was performed starting with II, R = NO_2, and recording the relatively slow appearance of I, a straight line with a different slope could be plotted (Fig. 1). As even in this case the slope should be

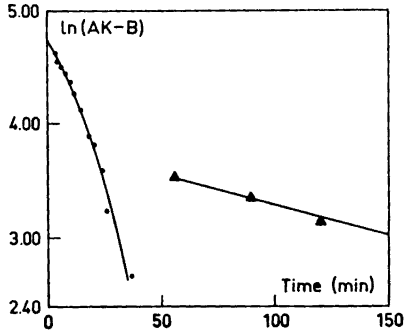
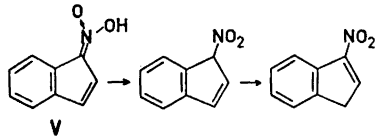


Fig. 1. Rate of equilibration of I, R = NO_2 (●), and II, R = NO_2 (▲), in $CDCl_3$ at 34°C.

equal to $k_1 + k_2$, the temperature and solvent being the same, this erratic result needs an explanation.

One may ask what the catalyst is in these cases. The most probable answer seems to be that water, present in small amounts in the compounds, is responsible for the catalytic effect. That would explain why different values for $k_1 + k_2$ were obtained depending on which of the tautomers was the reactant, since the content of water is not necessarily the same in the two compounds.



V

In this context it may be of interest to note that the nitronic acid V (the *aci*-form of 1-nitroindene) undergoes a ready conversion to 3-nitroindene *via* 1-nitroindene in deuterochloroform in the absence of added base.[19] Also in this case traces of water were postulated as catalyst.

In any case, whatever the catalyst may be, the results clearly indicate an appreciable rate enhancement in the tautomerism studied here, compared with the tautomerism in the 5-methyl system.[2] This gives support to the assumption that resonance structure III plays an important role in the anion part of the ion-pair. In other words, the prototropy involves a transition state with a high degree of negative charge on the 5-carbon, stabilized inductively and/or mesomerically by the nitro group. This result is in accordance with extended Hückel calculations carried out for the base-catalyzed tautomeric rearrangements in indenes,[20] and also with the recently discovered acetyl group migration to a nitro oxygen in 3-acetoxy-2-nitroindene.[21]

Efforts to detect small amounts of the nitronic acid IV in the equilibrium mixture by NMR were in vain. Apparently this molecule is of too high an energy to allow its existence in concentrations detectable by this method. This may be seen as a parallel to the thermodynamic instability of V, as visualized above.

Preliminary experiments aimed at isolating derivatives of IV have so far met with little success. By carrying out the tautomeric conversions in the presence of acylating agents, it was expected that *O*-acyl derivatives would be formed. Impetus to carry out such experiments came from the above-mentioned intra-molecular acetylation in 3-acetoxy-2-nitroindene.[21] Thus far acetic anhydride and benzoyl chloride have been tried, even with added base (pyridine or triethylamine). However, no characterizable substances have been isolated. With bases the system undergoes extensive decomposition.

This work confirms the assumption that the substituent in the 5-position plays a minor role in determining the position of the double bond in these systems. When $R = CH_3$, $K = 3.2$ (at 32°C) and with $R = NO_2$, $K = 2.3$ (at 34°C). This means that the 4H-cyclopenta[b]thiophene system is about 0.5 – 0.7 kcal/mol more stable (lower $G°$-value) than the 6H-cyclopenta[b]thiophene system at these temperatures.

EXPERIMENTAL

2-(β-Nitrovinyl)-3-thiophenealdehyde. To a mixture of 24 g (0.13 mol) of 2-formyl-3-thiophenealdehyde ethylene acetal [6] and 8.0 g (0.13 mol) of nitromethane in 100 ml of methanol cooled to 0 – 5°C, 40 ml of 40 % methanolic potassium hydroxide was added with stirring at such a rate that the temperature did not rise above 5°C. When the addition was complete, the stirring was continued for another half hour. Then the reaction mixture was poured onto concentrated hydrochloric acid and ice with vigorous stirring. A yellow solid separated, and this product was rapidly filtered, washed with water and dried. This gave 22 g of yellow powder, the NMR spectrum of which showed it to be a mixture of the title compound and its ethylene acetal produced in about equal amounts. This mixture was used directly in the next step. In order to perform a characterization, a small portion was hydrolysed with ethanolic hydrochloric acid and water, affording the pure title compound after crystallization from ethanol/water, m.p. 135.0 – 136.5°C. NMR (DMSO-d_6): τ_{CHO} = −0.2 ppm (s), τ_α = 1.20 ppm (d), τ_β = 1.87 ppm (d), τ_5 = 2.05 ppm (d), τ_4 = 2.35 ppm (d); J_{45} = 5.2 Hz, $J_{\alpha\beta}$ = 13.5 Hz. [Found: C 45.90; H 2.98; S 17.74. Calc. for $C_7H_5NO_3S$ (183.2): C 45.89; H 2.75; N 7.65; S 17.51.]

3-(β-Nitrovinyl)-2-thiophenealdehyde. Starting with 3-formyl-2-thiophenealdehyde ethylene acetal,[7] the same procedure as above gave a mixture of the title compound and its ethylene acetal. A small part of this crude mixture was hydrolyzed to yield the pure title compound as yellow needles from ethanol, m.p. 123 – 124°C. NMR (DMSO): τ_{CHO} = −0.3 ppm (s), τ_α = 1.35 ppm (d), τ_β = 1.73 ppm (d), τ_5 = 1.84 ppm (d), τ_4 = 2.18 ppm (d); J_{45} = 5.2 Hz, $J_{\alpha\beta}$ = 13.5 Hz. [Found: C 45.9; H 2.93; S 17.6. Calc. for $C_7H_5NO_3S$ (183.2): C 45.89; H 2.75; N 7.65; S 17.51.]

2-(β-Nitrovinyl)-3-thiophenealdehyde ethylene acetal. When the mixture consisting of 2-(β-nitrovinyl)-3-thiophenealdehyde and its ethylene acetal (the title compound) was refluxed in benzene solution with excess ethylene glycol and *p*-toluene sulfonic acid as catalyst and with azeotropic removal of water, a quantitative conversion to the title compound was achieved. Crystallization from ethanol afforded yellow prisms, m.p. 112 – 113°C. NMR (DMSO): τ_α = 1.60 ppm (d), τ_β = 2.18 ppm (d), τ_5 = 2.16 ppm (d), τ_4 = 2.78 ppm (d), $\tau_{CH_2,acetal}$ = 3.88 ppm (s), $\tau_{CH_3,acetal}$ = 5.95 ppm (s); J_{45} = 5.1 Hz, $J_{\alpha\beta}$ = 13.4 Hz. [Found: C 47.72; H 3.94; S 14.18. Calc. for $C_9H_9NO_4S$ (227.2): C 47.57; H 3.99; N 6.17; S 14.11.]

3-(β-Nitrovinyl)-2-thiophenealdehyde ethylene acetal. When the mixture of 3-(β-nitrovinyl)-2-thiophenealdehyde and its ethylene acetal (the title compound) was subjected to the same treatment as above, the title compound could be obtained in high yield (> 95 %). Yellow prisms were produced by crystallization from ethanol, m.p. 134 – 135°C. NMR (DMSO): τ_α = τ_β = 1.88 ppm (s), τ_5 = τ_4 = 2.36 ppm (s), $\tau_{CH_2,acetal}$ = 3.57 ppm (s), $\tau_{CH_3,acetal}$ = 5.95 ppm (s). [Found: C 48.00; H 4.16; S 14.1. Calc. for $C_9H_9NO_4S$ (227.2): C 47.57; H 3.99; N 6.17; S 14.11.]

2-(β-Nitroethyl)-3-thiophenealdehyde. To a solution of 5.0 g (0.13 mol) of sodium borohydride in 100 ml of ethanol, 12.0 g (0.0528 mol) of 2-(β-nitrovinyl)-3-thiophenealdehyde ethylene acetal in 200 ml of ethanol was added with stirring. The temperature was kept at 20 – 40°C during the addition; some cooling was necessary to maintain this temperature. After 3 h at room temperature, half of the volume of ethanol was evaporated under reduced pressure. The residue was carefully treated with acetic acid until the effervescence had ceased, and then 200 ml of 5 N hydrochloric acid was added. After 30 min at room temperature, the organic product was taken up in ether, washed with aqueous sodium bicarbonate and water and then dried ($MgSO_4$). Evaporation of the solvent gave 8.7 g (89 %) of the crude title compound as a brown oil. Rapid elution with ether through alumina gave the product as a light brown oil in a purity better than 95 % (NMR). NMR ($CDCl_3$): τ_{CHO} = 0.03 ppm (s), τ_4 = 2.56 ppm (d), τ_5 = 2.77 ppm (d), τ_α = 5.28 ppm (t), τ_β = 6.17 ppm (t); J_{45} = 5.5 Hz, $J_{\alpha\beta}$ = 6.7 Hz. IR (neat): 1680 cm^{-1} (strong, C=O) and 1555 cm^{-1} (strong, NO_2).

3-(β-Nitroethyl)-2-thiophenealdehyde. Method A. On treatment of 7.0 g (0.031 mol) of 3-(β-nitrovinyl)-2-thiophenealdehyde ethylene acetal with sodium borohydride according to the preceding procedure, 4.5 g (79 %) of the crude title compound was obtained as an oil. When dissolved in chloroform/hexane (and treated with charcoal), this product precipitated out as yellow crystals melting at 47.5 – 48.5°C on keeping overnight in the refrigerator. NMR ($CDCl_3$): τ_{CHo} = 0.00 ppm (s), τ_5 = 2.23 ppm (d), τ_4 = 2.86 ppm (d),

$\tau_\alpha = 5.27$ ppm (t), $\tau_\beta = 6.30$ ppm (t); $J_{45} = 5.0$ Hz, $J_{\alpha\beta} = 6.8$ Hz. IR (neat): 1655 cm^{-1} (s, C=O) and 1560 cm^{-1} (s, NO_2). [Found: C 45.5; H 3.89; N 7.53; S 17.6 Calc. for $C_7H_7NO_3S$ (185.2): C 45.39; H 3.81; N 7.56; S 17.32.]

Method B. 4.5 g (0.020 mol) of 3-(β-nitrovinyl)-2-thiophenealdehyde ethylene acetal was dissolved in 50 ml of acetone. A suspension of 0.400 g of tris(triphenylphosphine)rhodium chloride in 50 ml of benzene was added. The mixture was hydrogenated in a Parr apparatus at 3 – 4 atm. of initial pressure for 24 h at 50°C. The mixture was then rapidly passed through silica gel and the solvent evaporated. The residue was treated with ethanol and aqueous hydrochloric acid to effect hydrolysis of the acetal group. The product was worked up by extraction (ether), washing (bicarbonate and water) and drying ($MgSO_4$). This gave 2.0 g (55 %) of a brown oil with an IR spectrum almost identical with the spectrum of the title compound prepared according to method A.

5-Nitro-6H-cyclopenta[b]thiophene. To a solution of 7 g of potassium hydroxide in 100 ml of methanol, 7.0 g (0.038 mol) of 2-(β-nitroethyl)-3-thiophenealdehyde dissolved in 100 ml of methanol was added dropwise with stirring. The temperature was kept at 0 – 5°C throughout the addition by external cooling with ice-water. When the addition was complete, the stirring was continued for an additional 30 min and then the reaction mixture was poured onto 5 N hydrochloric acid and ice with vigorous stirring. A yellow solid almost immediately precipitated out. As this solid rapidly became dark in colour, it was as fast as possible filtered by suction and washed with water. After drying in a vacuum desiccator, the product could be kept in the refrigerator for more than a year without any sign of decomposition. In this way 4.5 g (71 %) of crude product, melting with decomposition at 100 – 110°C, was obtained. Crystallization from chloroform/hexane afforded (refrigerator) yellow prisms, m.p. 110°C (dec.). The NMR spectrum revealed the existence of two components, namely the title compound and its tautomer, 5-nitro-4H-cyclopenta[b]thiophene, in a ratio which changed with time, but which at equilibrium ($CDCl_3$, 34°C) was 30 : 70. The NMR data of the latter are given below in connection with the description of its independent synthesis. NMR ($CDCl_3$): *5-nitro-6H-cyclopenta[b]thiophene:* $\tau_4 = 2.14$ ppm (t), $\tau_2 = 2.62$ ppm (d), $\tau_3 = 2.86$ ppm (d), $\tau_6 = 6.03$ ppm (d); $J_{23} = 5.0$ Hz, $J_{46} = 2.0$ Hz.

5-Nitro-4H-cyclopenta[b]thiophene. Starting from 4.5 g (0.024 mol) of 3-(β-nitroethyl)-2-thiophenealdehyde, following the procedure described above, afforded 3.0 g (78 %) of the crude title compound melting at 80 – 90°C with decomposition. Crystallization from chloroform/hexane gave yellow to brown leaflets, m.p. 85°C (dec.). NMR ($CDCl_3$): $\tau_6 = 2.06$ ppm (t), $\tau_2 = 2.38$ ppm (d), $\tau_3 = 2.86$ ppm (d), $\tau_4 = 6.16$ ppm (d); $J_{23} = 4.9$ Hz, $J_{46} = 1.9$ Hz. [Found: C 50.1; H 3.12; N 8.22; S 19.0. Calc. for $C_7H_7NO_2S$ (167.2): C 50.28; H 3.01; N 8.38; S 19.19.]

The melting points are uncorrected. The IR spectra were recorded on a Perkin Elmer grating infrared spectrophotometer type 257, the NMR spectra on a Varian A 60 (with TMS as an internal standard). The elementary analyses were carried out at the Analytical Department, Chemical Center, University of Lund.

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