

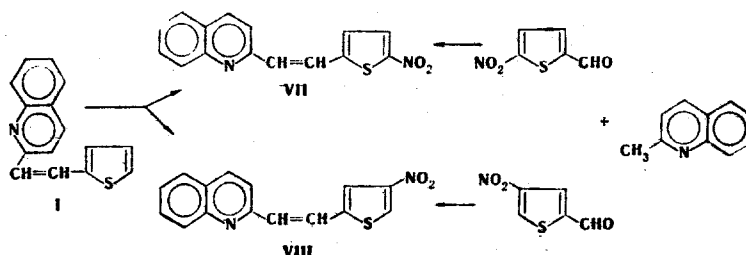
ELECTRONIC STRUCTURE AND REACTIVITY OF 2-[2-(4-R-2-QUINOLYL)VINYL]THIOPHENES AND 5-[2-(4-R-2-QUINOLYL)VINYL]-2,2'- BITHIOPHENES

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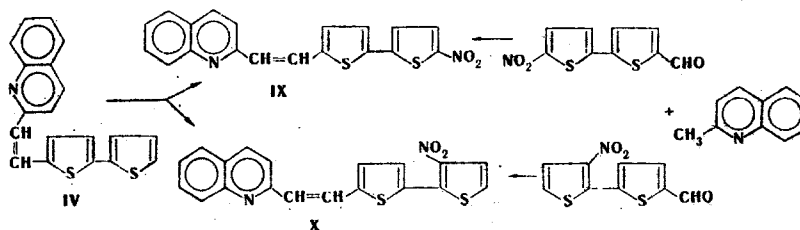
We have developed published work on the electrophilic substitution of quinoline derivatives of thiophene and 2,2'-bithiophene [1-3] with an examination of the nitration and formylation of 2-[2-(4-R-2-quinolyl)vinyl]-thiophenes [R = H (I), COOH (II), COOC₂H₅ (III)] and 5-[2-(4-R-2-quinolyl)vinyl]-2,2'-bithiophenes [R = H (IV), COOH (V), COOC₂H₅ (VI)].

Nitration of 2-[2-(2-quinolyl)vinyl]thiophene (I) with nitric acid (d 1.5) in acetic anhydride formed compounds (VII) and (VIII). We verified the structures of the synthetic mononitro compounds by independent synthesis (condensation of quinaldine with the appropriate nitro derivatives of thiophenecarboxaldehyde).

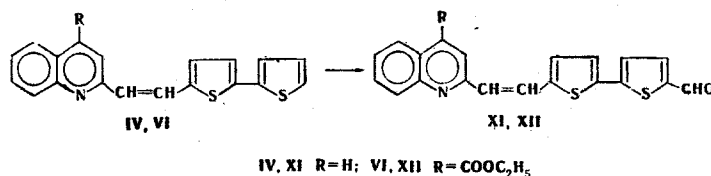


We attempted to formylate 2-[2-(4-R-2-quinolyl)vinyl]thiophenes (I)-(III) with dimethylformamide in the presence of excess phosphorus oxychloride (molar ratio 10:1) at 100°C for 7-8 h, but were unable to isolate the aldehydes.

Nitration of 5-[2-(2-quinolyl)vinyl]-2,2'-bithiophene (IV) with nitric acid (d 1.5) in acetic anhydride gave a mixture of two mononitro compounds, 5-[2-(2-quinolyl)vinyl]-5'-nitro-2,2'-bithiophene (IX) and 5-[2-(2-quinolyl)vinyl]-3'-nitro-2,2'-bithiophene (X), which we synthesized independently by condensation of the nitroaldehyde with quinaldine:



Formylation of 5-[2-(4-R-2-quinolyl)vinyl]-2,2'-bithiophenes (R = H, COOC₂H₅) with dimethylformamide in the presence of phosphorus oxychloride generated monocarbonyl compounds:



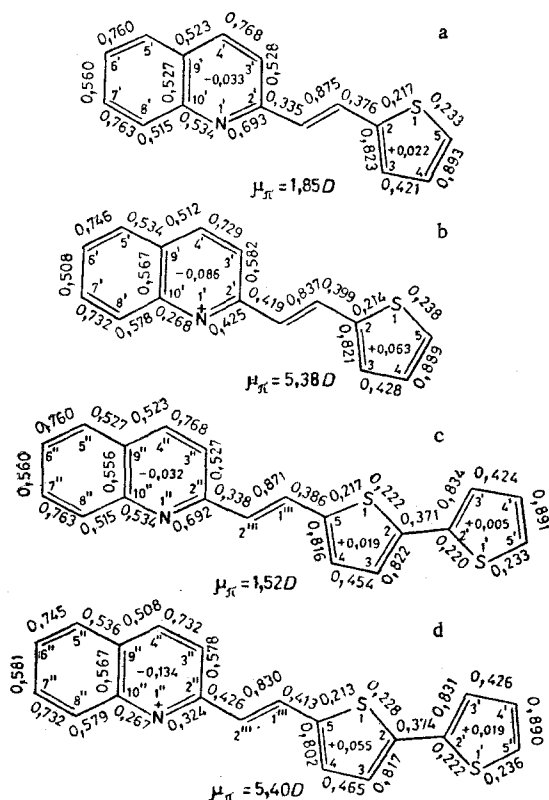
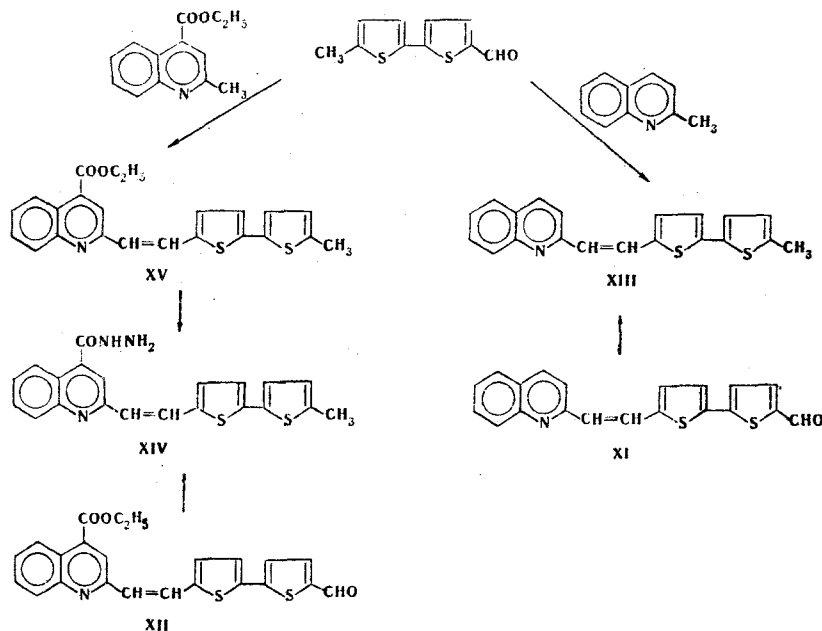


Fig. 1. Molecular diagrams of the neutral and protonated forms of a,b) 2-[2-(4-R-2-quinolyl)vinyl] derivatives of thiophene and c,d) 2,2'-bithiophene.

We verified the structures of (XI) and (XII) by independent synthesis:



We verified the identity of the compounds derived by direct nitration and formylation and by independent synthesis of TLC and IR and PMR spectroscopy.

We also made a quantum-chemical study of the reactivity of 2-[2-(4-R-2-quinolyl)vinyl]thiophenes (I)-(III) and their 2,2'-bithiophene analogs. We have justified our computational method and choice of parameters earlier in work on thiophene and 2,2'-bithiophene derivatives of quinoline [4].

Figure 1 shows the molecular diagrams of the compounds. Table 1 summarizes the calculated localization energies of the unsubstituted carbon atoms in the most reactive fragment of the molecule, the α -unsubstituted thiophene ring. Since the reactions in question take place in a strongly proton-donating medium, we thought it relevant to examine the reactivity indices of the species protonated at the ring nitrogen, (I')-(VI').

Analysis of the molecular diagrams reveals that the α -unsubstituted thiophene ring has a net positive charge and the quinoline fragment a net negative charge. Transfer of electron density from the thiophene ring to the quinoline fragment, particularly in the protonated species, could account for the deactivating effect of the quinoline fragment on the thiophene ring in electrophilic substitution reactions. Analysis of the relative reactivity of the carbon atoms of the thiophene ring is more properly couched in terms of the localization energies. The α -position of thiophene is most reactive, which is consistent with the experimental results. Evaluation of the relative reactivities of the entire series of compounds from the localization energy of the $C_{(5)}(C_{5'})$ atom of thiophene, as the most reactive reaction center, reveals that the bithiophene compounds are more reactive than their thiophene analogs. The same conclusion follows from generalization of the experimental results.

EXPERIMENTAL

Spectra were recorded on: IR: a UR-20 in KBr tables; PMR: a Hitachi-Perkin-Elmer R-22 (90 MHz) in DMSO- d_6 solution, internal standard tetramethylsilane (TMS); and UV: an SF-16 in ethanol solutions.

2-[2-(2-Quinolyl)vinyl]thiophene (I) was prepared by the method of [5]. Equimolar quantities (0.03 mole) of 2-thiophenecarboxaldehyde and quinaldine were heated in acetic anhydride (6 ml) for 1 h to 1 h 30 min. The cold solution was poured into 20% sodium carbonate solution (30 ml) with ice. The precipitate was filtered off and washed with water. The yield was 54%, mp 90-91°C (from ethanol). Found: C 76.3; H 4.7; N 5.8%. $C_{15}H_{11}NS$. Calculated: C 76.0; H 4.7; N 5.9%. IR spectrum: 960 cm^{-1} (trans CH=CH). UV spectrum, λ_{max} (log ϵ): 259 (4.31), 308 nm (4.35). PMR spectrum: 7.09 ppm (1H, d, J = 15.5 Hz, vinylic proton).

5-[2-(2-Quinolyl)vinyl]-2,2'-bithiophene (IV) was prepared in the same way as (I). The yield was 78%, mp 156-158°C (from ethanol). Found: C 71.8; H 4.0; N 4.3%. $C_{19}H_{13}NS_2$. Calculated: C 71.7; H 4.1; N 4.4%. IR spectrum: 960 cm^{-1} (trans CH=CH). PMR spectrum: 3-H 7.11; 4-H 7.13 ($J_{3,4}$ = 4 Hz); 5'-H 7.14; 3'-H 7.17; 4'-H 6.97 ($J_{3',4'} = J_{4',5'} = 4$ Hz); 7.84 and 7.02 ppm (J = 16 Hz) (vinylic protons). UV spectrum, λ_{max} (log ϵ): 220 (4.00), 260 (4.17), 314 (3.93), and 3.90 nm (3.65).

5-[2-(4-Ethoxycarbonyl-2-quinolyl)vinyl]-2,2'-bithiophene (VI) was prepared in the same way as (I). The yield was 52%, mp 131°C (from isopropanol). Literature: mp 130-131°C (from ethanol). UV spectrum, λ_{max} (log ϵ): 220 (4.52), 270 (4.16), 336 (4.20), and 414 nm (4.09).

Nitration of 2-[2-(2-Quinolyl)vinyl]thiophene (I). To acetic anhydride (30 ml), cooled to -5°C, was added nitric acid (d 1.5; 19 g, 0.30 mole). Compound (I) (4.4 g, 0.019 mole) was added portionwise with stirring to the resulting nitrating mixture at -15°C. The mixture was kept at -15°C for 3 h and then poured onto ice (150 g). The precipitated crystals were filtered off, washed with water, and dried. The yield was 4.7 g (89%). Fractional recrystallization (from ethanol-acetone) gave i) (VII) (3.8 g, 56.8%) with mp 201°C; [found: C 63.5; H 3.3; N 9.4%. $C_{15}H_{10}N_2O_2S$. Calculated: C 63.8; H 3.5; N 9.9%. IR spectrum: 1335, 1506 (NO_2) 959 cm^{-1} (trans CH=CH). UV spectrum, λ_{max} (log ϵ): 248 (4.27), 288 (4.42), 332 nm (4.45)]. ii) (VIII) (0.2 g, 1.9%) with mp 206°C; [found: C 63.5; H 3.3; N 9.4%. $C_{15}H_{10}N_2O_2S$. Calculated: C 63.8; H 3.5; N 9.9. IR spectrum: 1335, 1549 (NO_2), 955 cm^{-1} (trans CH=CH). UV spectrum, λ_{max} (log ϵ): 247 (4.18) and 305 nm (4.21)].

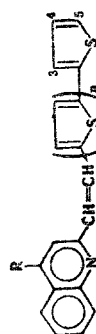
5-Nitro-2-thiophenecarboxaldehyde was prepared by the method of [6], mp 76-77°C. Literature [6]: mp 77°C. PMR spectrum (in acetone), δ , ppm: 3-H 6.02, 4-H 6.15, HCHO 8.12, $J_{3,4}$ = 4.5 Hz, in agreement with literature data [7].

5-Nitro-2-[2-(2-quinolyl)vinyl]thiophene (VII) was prepared by condensation of 5-nitro-2-thiophenecarboxaldehyde with quinaldine in the same way as (I). The yield was 4.8 g (90%), mp 201.5°C (from ethanol-acetone). IR spectrum: 1335, 1506 (NO_2), 959 cm^{-1} (trans CH=CH). UV spectrum, λ_{max} (log ϵ): 248 (4.27), 288 (4.42), and 332 nm (4.45).

4-Nitro-2-thiophenecarboxaldehyde was prepared by the method of [8], mp 55-56°C. Literature [8]: mp 55.5-56°C.

4-Nitro-2-[2-(2-quinolyl)vinyl]thiophene (VIII) was prepared by condensation of 4-nitro-2-thiophenecarboxaldehyde with quinaldine in the same way as (I). The yield was 62%, mp 206°C (from ethanol-acetone). IR spectrum: 1335, 1549 (NO_2), 955 cm^{-1} (trans CH=CH). UV spectrum, λ_{max} (log ϵ): 247 (4.18) and 305 nm (4.21). PMR spectrum: 7.22 ppm (1H, J = 16.0 Hz, vinylic proton).

TABLE 1. Calculated and Experimental Reactivity Indices of the Compounds



| Compound No. | Compound | | L_E , eV | | | Orientation of Se | Nitrogen | | Formylation | | | Yield of reaction products, % | |
|--------------|-----------------|---------------------|---------------------------|---|----------|----------------------------|----------------------------|--|--------------|---------|-----|--|---------------|
| | neutral species | proto-nated species | R | n | atom no. | neutral species | proto-nated species | nitration mixture | amount, mole | time, h | °C | nitration | formylation |
| I | I' | | H | 0 | 3 | 11,310 12,738 10,425 | 11,455 12,782 10,526 | HNO_3 (1,5) $(\text{CH}_3\text{CO})_2\text{O}$ | 15 | 3 | -15 | 5- NO_2 , 56.8 4- NO_2 1.9 | |
| II | II' | | COOH | 0 | 3 | 11,384 12,802 10,493 | 11,509 * 10,571 | * | excess | 7 | 96 | — | — |
| III | III' | | COOC_2H_5 | 0 | 3 | 11,375 12,797 10,485 | 11,491 † 10,562 | * | excess | 7 | 96 | — | — |
| IV | IV' | | H | 1 | 3' | 10,869 12,622 9,810 | 10,945 † 9,872 | HNO_3 (1,5) $(\text{CH}_3\text{CO})_2\text{O}$ | 4 | 4 | -10 | 5'- NO_2 , 53.6 3'- NO_2 , 22.3 | 5'-CHO; 60 |
| V | V' | | COOH | 1 | 3' | 10,929 † 9,864 | 10,989 † 9,913 | * | excess | 1 | 60 | — | — |
| VI | VI' | | COOC_2H_5 | 1 | 3' | 10,903 † 9,859 | 10,982 † 9,907 | * | excess | 1 | 60 | 5'-CHO; 61 | |

* Nitration not carried out.

† Self-consistency was not reached for the molecular fragment when the electron pair was localized on this atom.

‡ Formylation not carried out.

Nitration of 5-[2-(2-Quinoly)vinyl]-2,2'-bithiophene (IV). Nitric acid (d 1.5; 0.6 ml, 0.014 mole) was added dropwise to a solution of (IV) (1 g, 0.003 mole) in acetic anhydride (60 ml) with cooling to -10°C . The mixture was kept at -10°C for 4 h and then poured onto ice. The precipitate was filtered off, washed with water, and dried. The yield was 0.95 g (84.8%). Fractional recrystallization (from ethanol-acetone) gave i) (IX) (0.6 g, 53.6%) with mp 218°C ; [found: C 71.6; H 6.7; N 8.7%. $\text{C}_{19}\text{H}_{12}\text{N}_2\text{O}_2\text{S}_2$. Calculated: C 71.5; H 6.6; N 8.8%. IR spectrum: 1345 and 1490 cm^{-1} (NO_2). PMR spectrum: 7.20 ppm (1H, $J = 15.5\text{ Hz}$, vinylic proton). UV spectrum, λ_{max} (log ϵ): 236 (5.04), 274 (5.12), 315 (5.10), 442 nm (4.94)]. ii) (X) (0.25 g, 22.3%) with mp 180°C ; [found: C 71.4; H 6.7; N 8.8%. $\text{C}_{19}\text{H}_{12}\text{N}_2\text{O}_2\text{S}_2$. Calculated: C 71.5; H 6.6; N 8.8%. IR spectrum: 1335, 1525 (NO_2), 962 cm^{-1} (trans $\text{CH}=\text{CH}$). PMR spectrum: 7.20 ppm (1H, $J = 15.5\text{ Hz}$, vinylic proton). UV spectrum, λ_{max} (log ϵ): 242 (5.00), 291 (5.09), 312 (5.06), and 391 nm (5.02)].

5'-Nitro-5-formyl-2,2'-bithiophene was prepared by the method of [9], mp 196°C . Literature [9]: mp 196°C . PMR spectrum: 7.88 (4-H), 7.59 (3-H), 7.83 (3-H), 9.75 ppm (HCHO), $J_{4',5'} = 4.5$, $J_{3,4} = 4.0\text{ Hz}$, in agreement with literature data [9].

5'-Nitro-5-[2-(2-quinoly)vinyl]-2,2'-bithiophene (IX) was prepared in the same way as (I). The yield was 82%, mp $216\text{--}218^{\circ}\text{C}$ (from ethanol-acetone). IR spectrum: 1345, 1490 (NO_2), 963 cm^{-1} (trans $\text{CH}=\text{CH}$).

3'-Nitro-5-formyl-2,2'-bithiophene was prepared by the method of [10], mp 156°C . Literature [10], mp 156°C . PMR spectrum: 7.88 (4-H), 7.55 (3-H), 7.61 (4-H), 7.66 (5-H), 9.80 ppm (HCHO), $J_{5',4'} = 6.0$, $J_{3,4} = 42\text{ Hz}$.

3'-Nitro-5-[2-(2-quinoly)vinyl]-2,2'-bithiophene (X) was prepared in the same way as (I). The yield was 48%, mp 180°C (from ethanol-acetate). IR spectrum: 1335, 1525 (NO_2), 962 cm^{-1} (trans $\text{CH}=\text{CH}$).

Formylation of 5-[2-(4-Ethoxycarbonyl-2-quinoly)vinyl]-2,2'-bithiophene (VI). Dimethylformamide (5 ml) was added dropwise to cooled and stirred phosphorus oxychloride (2 ml, 0.020 mole). After 10 min, (VI) (0.5 g, 0.001 mole) was added while cooling was continued. The reaction mixture was stirred at room temperature for 10 min, then heated to 60°C for 1 h, and finally poured onto ice and neutralized with saturated sodium carbonate solution. The precipitate was filtered off and washed with water. The yield was 62%, mp 172°C (from ethanol-acetone). IR spectrum: 1732, 1670, 950 cm^{-1} . Found: C 65.6; H 4.2; N 3.3%. $\text{C}_{23}\text{H}_{17}\text{NO}_3\text{S}_2$. Calculated: C 65.9; H 4.1; N 3.3%. PMR spectrum: 7.25 (1H, $J = 15.5\text{ Hz}$, vinylic proton), 9.94s (1HCHO). UV spectrum, λ_{max} (log ϵ): 230 (4.11), 250 (4.08), 280 (3.93), 420 nm (4.70). Semicarbazone (XVI): mp 240°C (from acetone). IR spectrum: 1724 ($\text{C}=\text{O}$), 1690 (amide CO), 1632 cm^{-1} (NH_2). Found: C 64.3; H 4.5; N 12.5%. $\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}_3\text{S}_2$. Calculated: C 64.8; H 4.5; N 12.6%. Thiosemicarbazone (XVII): did not melt. IR spectrum: 17.24 ($\text{C}=\text{O}$), 1602 cm^{-1} ($\text{C}=\text{N}$). Found: C 62.8; H 4.4; N 12.2%. $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_2\text{S}_3$. Calculated: C 62.8; H 4.4; N 12.2%. Oxime (XVIII): did not melt. IR spectrum: 3260 (OH), 1610 cm^{-1} ($\text{C}=\text{N}$). Found: C 60.3; H 4.2; N 6.4%. $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_3\text{S}_2$. Calculated: C 60.8; H 4.2; N 6.4%. Hydrazone (XIX): did not melt. IR spectrum: 1600 ($\text{C}=\text{N}$), 1630 cm^{-1} (NH_2). Found: C 60.0; H 4.0; N 16.2%. $\text{C}_{21}\text{H}_{17}\text{N}_5\text{OS}_2$. Calculated: C 60.1; H 4.1; N 16.7%.

Formylation of 5-[2-(2-quinoly)vinyl]-2,2'-bithiophene (IV) was carried out in the same way as that of (VI). The yield was 61%, mp 180°C (from isopropanol-acetone). Found: C 68.7; H 3.8; N 4.0%. $\text{C}_{20}\text{H}_{13}\text{NOS}_2$. Calculated: C 69.1; H 3.8; N 4.0%. IR spectrum: 1670, 970 cm^{-1} . PMR spectrum: 7.26 (1H, $J = 16.0\text{ Hz}$, vinylic proton), 9.94s ppm (1HCHO). UV spectrum, λ_{max} (log ϵ): 240 (4.38), 330 (3.68), 380 (4.04), 420 nm (3.96). Semicarbazone (XX): mp 230°C (decomposition, from isopropanol-acetone). IR spectrum: 1698 ($\text{C}=\text{O}$), 1604 ($\text{C}=\text{N}$), 970 cm^{-1} ($\text{C}=\text{C}$). Found: C 62.0; H 4.0; N 13.8%. $\text{C}_{21}\text{H}_{16}\text{N}_4\text{OS}_2$. Calculated: C 62.4; H 4.0; N 13.8%. Thiosemicarbazone (XXI): did not melt. IR spectrum: 1608 ($\text{C}=\text{N}$), 970 cm^{-1} ($\text{C}=\text{C}$). Found: C 59.7; H 3.7; N 13.0%. $\text{C}_{21}\text{H}_{16}\text{N}_4\text{S}_3$. Calculated: C 60.0; H 3.8; N 13.3%. Oxime (XXII), mp 245°C (from aqueous pyridine). IR spectrum: 3300 (OH), 1604 cm^{-1} ($\text{C}=\text{N}$). Found: C 65.8; H 3.9; N 7.3%. $\text{C}_{20}\text{H}_{14}\text{N}_2\text{OS}_2$. Calculated: C 66.3; H 3.9; N 7.7%. Hydrazone (XXIII), mp 332°C (from dioxane). IR spectrum: 1596 ($\text{C}=\text{N}$), 1638 cm^{-1} (NH_2). Found: C 66.1; H 4.1; N 11.6%. $\text{C}_{20}\text{H}_{15}\text{N}_3\text{S}_2$. Calculated: C 66.5; H 4.1; N 11.6%.

5-Methyl-2,2'-bithiophene was prepared by the method of [11]. The yield was 75%, bp $139\text{--}140^{\circ}\text{C}$ (14 mm).

5-Methyl-5'-formyl-2,2'-bithiophene was prepared by the method of [11]. The yield was 93%, mp 98°C (from ethanol).

5-Methyl-5'-[2-(4-ethoxycarbonyl-2-quinoly)vinyl]-2,2'-bithiophene (XV) was prepared by the method of [5]. The yield was 82%, mp $94\text{--}96^{\circ}\text{C}$ (from ethanol). IR spectrum: 1700 ($\text{C}=\text{O}$), 2900 cm^{-1} (CH_3).

5-Methyl-5'-[2-(4-hydrazinocarbonyl-2-quinoly)vinyl]-2,2'-bithiophene (XIV) was prepared by the method of [12]. The yield was 42%, mp $206\text{--}208^{\circ}\text{C}$. IR spectrum: 1700 ($\text{C}=\text{O}$), 2900 cm^{-1} (CH_3). Found: C 66.7; H 4.2; N 10.5%. $\text{C}_{23}\text{H}_{17}\text{N}_3\text{OS}_2$. Calculated: C 66.5; H 4.1; N 10.1%.

Reduction of 5'-formyl-5-[2-(4-ethoxycarbonyl-2-quinolyl)vinyl]-2,2'-bithiophene (XII) was carried out by the method of [11], mp 206-208°C. IR spectrum: 1700 (amide CO), 2900 cm^{-1} (CH_3).

5'-Methyl-5-[2-(2-quinolyl)vinyl]-2,2'-bithiophene (XIII) was prepared by the method of [5]. The yield was 43%, mp 118-119°C (from isopropanol). IR spectrum: 2900 cm^{-1} (CH_3). Found: C 72.0; H 4.5; N 4.2%. $\text{C}_{20}\text{H}_{15}\text{NS}_2$. Calculated: C 72.2; H 4.5; N 4.2%.

Reduction of 5'-formyl-5-[2-(2-quinolyl)vinyl]-2,2'-bithiophene (XI) was carried out by the method of [11], mp 118-119°C (from isopropanol). IR spectrum: 2900 cm^{-1} (CH_3).

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SYNTHESIS AND STRUCTURE OF NITRO DERIVATIVES OF 4-(2-THIENYL)-3-BUTEN-2-ONE

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Combes, Hebbelynck, and Zedrut used concentrated nitric acid in acetic anhydride [1] and Pappalardo nitric acid in concentrated sulfuric acid [2] for the nitration of 4-(2-thienyl)-3-buten-2-one (I). They considered that only 4-(5-nitro-2-thienyl)-3-buten-2-one was formed rather than a mixture of the 4- and 5-nitro isomers, which would have been expected on the basis of the properties of carbonyl derivatives of thiophene [3]. Pappalardo [2] cited no evidence for his identification of the isolated compound with melting point 127°C as 4-(5-nitro-2-thienyl)-3-buten-2-one. Combes et al. [1] verified the structure of the synthetic 4-(5-nitro-2-thienyl)-3-buten-2-one with mp 131-131.5°C by conversion to 5-nitro-2-thiophenecarboxylic acid and deduced the trans orientation of the olefinic hydrogens from a calculation of its UV spectrum.

We have continued our work on the reactivity of α , β -unsaturated ketones of the thiophene series with a study of the nitration of 4-(2-thienyl)-3-buten-2-one (I) with potassium nitrate in concentrated sulfuric acid and with concentrated nitric acid in 1,2-dichloroethane. Nitration of compound (I) with potassium nitrate in concentrated sulfuric acid gave a mixture of the 5- and 4-nitro compounds in the ratio 2.6:1 (from the PMR parameters of the crude substance). Fractional recrystallization gave only one nitro ketone with melting point 131.5-132.5°C. We have so far not been able to isolate the second isomer in the pure form. Its PMR and IR parameters identified the isolated nitro ketone as 4-(5-nitro-2-thienyl)-3-buten-2-one (II) with the trans orientation of the hydrogen atoms at the double bond. We carried out an x-ray structure analysis of ketone (II) to find the bond angles and lengths and to decide between the O,S-cis or trans conformations. This revealed that

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