SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF $\pi$-EXTENDED N-ARYLPYRROLO[3,4-$d$]TETRATHIAFULVALENES

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Abstract - A series of $\pi$-extended N-arylpyrrolo[3,4-$d$]tetrathiafulvalenes, N-aryl-2-[4,5-bis(ethylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-$c$]pyrroles, (3a-d) were prepared via cross-coupling of 4,5-bis(ethylthio)-1,3-dithiol-2-one (12) with N-aryl-(1,3)-dithiolo[4,5-$c$]pyrrole-2-thiones (11a-d). The latters were obtained by the reactions of 4,5-bis(bromomethyl)-1,3-dithiole-2-thione (8) with aromatic amines (9a-d). Electrochemical behavior of compounds (3a-d) was studied by means of cyclic voltammetry. It was found that all these compounds (3a-d) have comparable to or lower half-wave potentials than those of N-alkyl-pyrrolo[3,4-$d$]tetrathiafulvalenes (2a-c).

INTRODUCTION

Tetrathiafulvalene (TTF) (1) is a reversible and stable two-electron-donating material and forms crystalline charge transfer complexes with a variety of acceptors, such as tetracyanoquinodimethane (TCNQ), tetracyanoethylene (TCNE), chloranil, and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ). These charge transfer complexes exhibit prominent conductivity of metallic character. Therefore, tetrathiafulvalene (1) has been a subject of great interest for about three decades due to its unique $\pi$-donating property.1 In order to obtain a high quality of organic conductors, molecular designs of new types of electron donors have been continuously investigated. One of the important strategies for the molecular designs is to extend $\pi$-conjugation to decrease on-site coulomb repulsion.2 A variety of pyrrole-fused tetrathifulvalene derivatives were prepared and provided good results.3,4 A new synthetic method of pyrrole-annulated tetrathiafulvalenes, N-alkylpyrrolo[3,4-$d$]tetrathiafulvalenes (2a-c), was accomplished by the reactions of 4,5-bis(bromomethyl)-1,3-dithiole-2-thione (8) with alphatic amines.5,6 However, there is no report on...
N-aryl-substituted pyrrolo[3,4-d]tetraethiafulvalenes which have a larger conjugation system.

In the present paper, we report the synthesis and properties of the promising electron-donors, N-aryl-2-[4,5-bis(ethylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithioolo[4,5-c]pyrroles (3a-d).

RESULTS AND DISCUSSION

Preparation of N-Aryl-(1,3)-dithioolo[4,5-c]pyrrole-2-thiones (11a-d).

As shown in Scheme 1, the starting material, 4,5-bis(bromomethyl)-1,3-dithiole-2-thione (8) was readily prepared according to the literature.\(^6\) When a solution of the 1,3-dithiole-2-thione (8) and an equimolar amount of aniline (9a) in tetrahydrofuran-acetonitrile (1:2 v/v) was refluxed for 3 h in the presence of potassium carbonate, N-phenyl-4,6-dihydro-(1,3)-dithioolo[4,5-c]pyrrole-2-thione (10a) and N-phenyl-(1,3)-dithioolo[4,5-c]pyrrole-2-thione (11a) were obtained in 40 and 1% yields, respectively. In a similar manner, the reactions of 1,3-dithiole-2-thione (8) with 4-methyl- and 4-methoxyanilines (9b,c) gave 10b,c (44 and 55%) and 11b,c (6 and 24%), respectively. The reaction with 4-chloroaniline (9d) gave 10d

\[\text{Scheme 1}\]
(19%) as the sole product. These results revealed that anilines having an electron-donating substituent gave good results, while electron-withdrawing chlorine atom retarded the reaction. It was found that the products (10a-d) having dihydropyrrole ring were major products. These compounds are unstable and susceptible to air oxidation. Compound (10d) were readily dehydrogenated with DDQ to afford 11d in 96% yield. Similarly, DDQ oxidation of compounds (10a-c) gave 11a-c in high yields.

![Scheme 2](image)

**Synthesis of N-Aryl-2-[4,5-bis(ethylthio)-1,3-dithiole-2-yldene]-(1,3)-dithiolo[4,5-c]-pyrroles (3a-d)**

Cross-coupling reaction of 4,5-bis(ethylthio)-1,3-dithiol-2-one (12) with N-aryl-(1,3)-dithiolo[4,5-c]-pyrrole-2-thiones (11a-d) in triethyl phosphtate at 130 °C gave N-aryl-2-[4,5-bis(ethylthio)-1,3-dithiole-2-yldene]-(1,3)-dithiolo[4,5-c]pyrroles (3a-d) in 8-42% yields. In these reactions, self-coupling reactions of compounds (11a-d) were not observed.

![Scheme 3](image)
Electrochemical Behavior of Compounds (11a-d) by Means of Cyclic Voltammetry

Oxidation potentials of $N$-aryl-pyrrolo[3,4-$d$]tetrathiafulvalenes (11a-d) were obtained by cyclic voltammetry and are summarized in Table 1. All the compounds showed two pairs of reversible redox waves, indicating good stabilities of the corresponding radical cations and dications in dichloromethane.

Table 1. Oxidation Potentials $E_{1/2}^{1}$ and $E_{1/2}^{2}$ of Compounds (2a-d) and (3a-d)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}^{1}$</th>
<th>$E_{1/2}^{2}$</th>
<th>$\Delta E_p$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>0.43</td>
<td>0.86</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>0.41</td>
<td>0.84</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td>0.43</td>
<td>0.85</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>3d</td>
<td>0.43</td>
<td>0.85</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>0.46</td>
<td>0.92</td>
<td>0.46</td>
<td>a</td>
</tr>
<tr>
<td>2b</td>
<td>0.43</td>
<td>0.87</td>
<td>0.44</td>
<td>a</td>
</tr>
<tr>
<td>2c</td>
<td>0.44</td>
<td>0.87</td>
<td>0.43</td>
<td>a</td>
</tr>
<tr>
<td>2d</td>
<td>0.44</td>
<td>0.87</td>
<td>0.43</td>
<td>a</td>
</tr>
</tbody>
</table>

a Ref. 6.

From these data, we can deduce that $N$-arylpyrrolo[3,4-$d$]tetrathiafulvalenes (11a-d) have comparable or lower first half-wave potentials than those of $N$-alkylpyrrolo[3,4-$d$]tetrathiafulvalenes (2a-d). In particular, compound (3b) gave the lowest first half-wave oxidation potential $E_{1/2}^{1}$ than those of any other ones. However, it was found that their electrochemical properties were not remarkably improved as compared with those of $N$-alkyl derivatives (2a-d).

CONCLUSION

$N$-Aryl-2-[4,5-bis(ethylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-c]pyrroles (3a-d) were prepared by cross-coupling of 4,5-bis(ethylthio)-1,3-dithiol-2-one (12) with $N$-aryl-(1,3)-dithiolo[4,5-c]pyrrole-2-thiones (11a-d). It was found that all these compounds (3a-d) have comparable to or lower half-wave potentials than those of $N$-alkyl-substituted pyrrolo[3,4-$d$]tetrathiafulvalenes (2a-c).
EXPERIMENTAL

The melting points were determined by capillary tube method and are uncorrected. The IR spectra were taken on a Varian FT-IR 1730 spectrophotometer. The $^1$H NMR spectra were recorded with a Bruker AV300 spectrometer (300 MHz). The MS spectra were obtained by a Hewlett Packard 1100-HPLC/MSD instrument. Cyclic voltammetry was carried out on a Potentiostat/Galvanostat 273A instrument employing 0.1M Bu$_4$PF$_6$ as the supporting electrode in dichloromethane, with sweep speed of 50 mV/s. The counter and working electrode were made of platinum and the reference electrode was Ag/AgCl.

All solvents were purified by standard methods and were purged with argon immediately before use. All reagents were obtained from ACROS or TCI and used without further purification. The starting material, 4,5-bis(bromomethyl)-1,3-dithiole-2-thione (8) was prepared by the reaction of ethylene dithiocarbonate (4) with dimethyl acetylenedicarboxylate (5) according to references. 4,5-Bis(ethylthio)-1,3-dithiol-2-one (12) was also obtained according to reference. All the reactions were carried out under dry argon atmosphere otherwise stated.

Reactions of 4,5-Bis(bromomethyl)-1,3-dithiole-2-thione (8) with Anilines (9a-d).

General Procedure: To a refluxing solution of 4,5-bis(bromomethyl)-1,3-dithiole-2-thione (8) (0.68-2.0 mmol) in tetrahydrofuran-acetonitrile 1:2 v/v (30-60 mL) was added aniline (9a-d) (0.68-2.0 mmol) in the presence of potassium carbonate (2.7-8.0 mmol). The mixed solution was additionally refluxed for 0.5-6 h. After removing the solvent in vacuo, a dichloromethane solution of the residue was washed with water and dried over magnesium sulfate. The organic solution was concentrated in vacuo and the crude product was chromatographed on a silica gel column with dichloromethane-petroleum ether (60-90 °C) 2:1 as the eluent to give N-aryl-4,6-dihydro-(1,3)-dithiole[4,5-c]pyrrole-2-thiones (10a-d) and N-aryl-(1,3)-dithiole[4,5-c]pyrrole-2-thiones (11a-c).

N-Phenyl-4,6-dihydro-(1,3)-dithiole[4,5-c]pyrrole-2-thione (10a) and N-Phenyl-(1,3)-dithiole[4,5-c]pyrrole-2-thione (11a). A solution of 4,5-bis(bromomethyl)-1,3-dithiole-2-thione (8) (320 mg, 1 mmol) and aniline (9a) (93 mg, 1 mmol) in tetrahydrofuran-acetonitrile 1:2 v/v (30 mL) was refluxed for 6 h in the presence of potassium carbonate (1.10 g, 8 mmol). After the treatment as described above, the crude product was chromatographed on a silica gel column with dichloromethane-petroleum ether (2:1). The first fraction gave N-phenyl-(1,3)-dithiole[4,5-c]pyrrole-2-thione (11a) as yellow solid, yield 3.1 mg (1%); mp 160.5-161.2 °C (from dichloromethane-petroleum ether (60-90 °C)); IR (KBr): ν 1593, 1502, 1048 cm$^{-1}$; $^1$H NMR (CDCl$_3$): $\delta$ 7.10 (2H, s, 4-6-H), 7.38-7.42 (3H, m, 3'-, 4'-5'-H), 7.48-7.53 (2H, m, 2'-6'-H); MS (APCI): m/z 250 ([M+1]$^+$). Anal. Calcd for C$_{11}$H$_7$NS$_3$: C, 52.98; H, 2.83; N, 5.62. Found: C, 52.99; H, 2.60; N, 5.55. The second fraction gave N-phenyl-4,6-dihydro-(1,3)-dithiole[4,5-c]pyrrole-2-thione (10a) as yellow solid, yield 100 mg (40%); mp 181 °C (from dichloromethane-petroleum ether (60-90 °C)); IR (KBr): ν 1602, 1504, 1345, 1212, 1052 cm$^{-1}$; $^1$H NMR (CDCl$_3$): $\delta$ 4.51 (4H, s, 4-CH$_2$, 6-CH$_2$), 6.59 (2H, d, $J = 8.6$ Hz, 3'-5'-H), 6.83 (1H, dd, $J = 8.6, 7.3$ Hz, 4'-H), 7.34 (2H, d, $J = 7.3$ Hz, 2'-6'-H). Anal. Calcd for C$_{11}$H$_9$NS$_3$: C, 52.55; H, 3.61;
N-(4-Methylphenyl)-4,6-dihydro-(1,3)-dithiol0[4,5-c]pyrrole-2-thione (10b) and N-(4-Methylphenyl)-(1,3)-dithiol0[4,5-c]pyrrole-2-thione (11b). A solution of compound (8) (960 mg, 3 mmol) and 4-methylaniline (9b) (321 mg, 3 mmol) in tetrahydrofuran-acetonitrile (1:2 v/v) (75 mL) was refluxed for 3 h in the presence of potassium carbonate (1.66 g, 12 mmol) and worked up as described above. The crude product was chromatographed on a silica gel column with dichloromethane-petroleum ether (60-90 °C) (2:1). The first fraction gave N-(4-methylphenyl)-(1,3)-dithiol0[4,5-c]pyrrole-2-thione (11b) as yellow solid, yield 51 mg (6%); mp 178 °C (decomp) (from dichloromethane-petroleum ether (60-90 °C)); 1H NMR (CDCl3): δ 2.42 (3H, s, CH3), 7.05 (2H, d, J = 7.8 Hz, 3’-5’-H), 7.25 (2H, s, 4-6-H), 7.28 (2H, d, J = 7.8 Hz, 2’-6’-H). Anal. Calcd for C12H9NS: C, 54.72; H, 3.44; N, 5.32. Found: C, 54.90; H, 3.24; N, 5.16. The second fraction gave N-(4-methylphenyl)-4,6-dihydro-(1,3)-dithiol0[4,5-c]pyrrole-2-thione (10b) as yellow solid, yield 344 mg (44%); mp 194-196 °C (from dichloromethane-petroleum ether (60-90 °C)); IR (KBr): ν 1611, 1515, 1366, 1049 cm⁻¹; 1H NMR (CDCl3): δ 2.30 (3H, s, CH3), 4.49 (4H, s, 4-CH2, 6-CH2), 6.50 (2H, d, J = 8.6 Hz, 3’-5’-H), 7.13 (2H, d, J = 8.6 Hz, 2’-6’-H). Anal. Calcd for C12H11NS: C, 54.30; H, 4.18; N, 5.28. Found: C, 54.12; H, 4.00; N, 5.34.

N-(4-Methoxyphenyl)-4,6-dihydro-(1,3)-dithiol0[4,5-c]pyrrole-2-thione (10c) and N-(4-Methoxyphenyl)-(1,3)-dithiol0[4,5-c]pyrrole-2-thione (11c). A solution of compound (8) (218 mg, 0.68 mmol) and 4-methoxyaniline (9c) (84 mg, 0.68 mmol) in tetrahydrofuran-acetonitrile (1:2 v/v) (30 mL) was refluxed for 30 min in the presence of potassium carbonate (376 g, 2.72 mmol) and worked up as described above. The crude product was chromatographed on a silica gel column with dichloromethane-petroleum ether (2:1). The first fraction gave N-(4-methoxyphenyl)-(1,3)-dithiol0[4,5-c]pyrrole-2-thione (11c) as yellow solid, yield 45 mg (24%); mp 187-187.5 °C (from dichloromethane-petroleum ether (60-90 °C)); IR (KBr): ν 2293, 1633, 1516, 1246, 1067 cm⁻¹; 1H NMR (CDCl3): δ 3.86 (3H, s, OCH3), 6.80 (2H, s, 4-6-H), 6.97 (2H, d, J = 8.6 Hz, 3’-5’-H), 7.26 (2H, d, J = 8.6 Hz, 2’-6’-H); MS (APCI): m/z 280 ([M+1]+). Anal. Calcd for C12H11NO3S: C, 51.58; H, 3.25; N, 5.01. Found: C, 51.90; H, 3.24; N, 5.11. The second fraction gave N-(4-methoxyphenyl)-4,6-dihydro-(1,3)-dithiol0[4,5-c]pyrrole-2-thione (10c) as yellow solid, yield 99 mg (55%); mp 188-190 °C (from dichloromethane-petroleum ether (60-90 °C)); IR (KBr): ν 1629, 1518, 1326, 1243, 1052 cm⁻¹; 1H NMR (CDCl3): δ 3.77 (3H, s, OCH3), 4.44 (4H, s, 4-CH2, 6-CH2), 6.51 (2H, d, J = 8.8 Hz, 3’-5’-H), 6.89 (2H, d, J = 8.8 Hz, 2’-6’-H); MS (APCI): m/z 282 ([M+1]+). Anal. Calcd for C12H11NO3S: C, 51.21; H, 3.94; N, 4.98. Found: C, 51.12; H, 4.00; N, 4.88.

N-(4-Chlorophenyl)-4,6-dihydro-(1,3)-dithiol0[4,5-c]pyrrole-2-thione (10d). A solution of compound (8) (640 mg, 2.0 mmol) and 4-chloroaniline (9d) (255 mg, 2.0 mmol) in tetrahydrofuran-acetonitrile (1:2 v/v) (60 mL) was refluxed for 3 h in the presence of potassium carbonate (1.1 g, 8.0 mmol) and worked up as described above. The crude product was chromatographed on a silica gel column with
dichloromethane-petroleum ether (2:1) to give N-(4-chlorophenyl)-(1,3)-dithiolo[4,5-c]pyrrole-2-thione (10d) as yellow solid, yield 108 mg (19%); mp 199 °C (decomp) (from dichloromethane-petroleum ether (60-90°C)); IR (KBr): ν 1595, 1498, 1369, 1056 cm⁻¹; ¹H NMR (CDCl₃): δ 4.50 (4H, s, 4-CH₂, 6-CH₂), 6.50 (2H, d, J = 9.0 Hz, 2'-6'-H), 7.26 (2H, d, J = 9.0 Hz, 3'-5'-H). Anal. Calcd for C₁₁H₈NCIS₃: C, 46.22; H, 2.82; N, 4.90. Found: C, 46.53; H, 2.72; N, 4.99.

Preparation of N-Aryl-(1,3)-dithiolo[4,5-c]pyrrole-2-thiones (11a-d): N-(4-Chloro-phenyl)-(1,3)-dithiolo[4,5-c]pyrrole-2-thione (11d). To a solution of N-(4-chlorophenyl)-4,6-dihydro-(1,3)-dithiolo[4,5-c]pyrrole-2-thione (10d) (158 mg, 0.55 mmol) in chloroform (20 mL) was dropwise added DDQ (125 mg, 0.55 mmol) in benzene (20 mL) in a period of 1 h at -15 to -10 °C. After being allowed to stand for 1 h, the reaction mixture was filtrated and the evaporation residue was dissolved in dichloromethane (50 mL). The solution was washed with brine (50 mL x 2) and water (50 mL x 2) and concentrated to give N-(4-chlorophenyl)-(1,3)-dithiolo[4,5-c]pyrrole-2-thione (11d) as yellow solid, yield 150 mg (96%); mp 180 °C (from dichloromethane dichloromethane-petroleum ether (60-90 °C)); IR (KBr): ν 1644, 1498, 1314, 1068 cm⁻¹; ¹H NMR (CDCl₃): δ 7.06 (2H, s, 4-6-H), 7.34 (2H, d, J = 8.7 Hz, 2'-6'-H), 7.48 (2H, d, J = 8.7 Hz, 3'-5'-H). Anal. Calcd for C₁₁H₈NCIS₃: C, 46.55; H, 2.13; N, 4.94. Found: C, 46.50; H, 2.33; N, 4.89.

N-Aryl-(1,3)-dithiolo[4,5-c]pyrrole-2-thiones (11a-c). In a similar manner, compounds (11a-c) were obtained from the corresponding 4,6-dihydro derivatives (10a-c) in yields of 66, 83, 83%, respectively.

Preparation of N-aryl-2-[4,5-bis(ethylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-c]pyrroles (3a-d). General Procedure: A mixture of 4,5-bis(ethylthio)-1,3-dithiol-2-one (12) (238 mg, 1.0 mmol) and N-aryl-(1,3)-dithiolo[4,5-c]pyrrole-2-thione (11a-d) (1.0 mmol) in triethyl phosphate (4 mL) was heated for 3 h at 130 °C. The reaction mixture changed from suspension to a red-colored solution in the meantime. After being cooled to room temperature, the precipitate was collected by filtration and washed with methanol to give N-aryl-2-[4,5-bis(ethylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-c]pyrroles (3a-d).

N-Phenyl-2-[4,5-bis(ethylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-c]pyrrole (3a). This compound was obtained from the reaction with 11a as yellow solid, yield 183 mg (42%); mp 170-171.5 °C (from dichloromethane dichloromethane-petroleum ether (60-90 °C)); IR (KBr): ν 1597, 1512 cm⁻¹; ¹H NMR (CDCl₃): δ 1.34 (3H, t, J = 7.4 Hz, CH₃), 2.89 (2H, q, J = 7.4 Hz, CH₂), 6.91 (2H, s, 4-6-H), 7.20-7.35 (3H, m, 3'-4'-5'-H), 7.44 (2H, d, J = 8.5 Hz, 2'-6'-H); MS (APCI): m/z 440 ([M+1]+). Anal. Calcd for C₁₈H₁₇NS₄: C, 49.16; H, 3.90; N, 3.19. Found: C, 49.16; H, 3.94; N, 3.02.
N-(4-Methylphenyl)-2-[4,5-bis(ethylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-c]-pyrrole (3b). This compound was obtained from the reaction with 11b as yellow solid, yield 90 mg (20%); mp 150.5-151.5 °C (from dichloromethane dichloromethane-petroleum ether (60-90 °C)) ; IR (KBr): ν 1620, 1524 cm⁻¹; ¹H NMR (CDCl₃): δ 1.34 (3H, t, J = 7.3 Hz, CH₃), 2.88 (2H, q, J = 7.3 Hz, CH₂), 6.87 (2H, s, 4-6-H), 7.22 (2H, s, 3'-5'-H), 7.28 (2H, s, 2'-6'-H); MS (APCI): m/z 454 ([M+1]). Anal. Calcd for C₁₉H₁₅NS₆: C, 50.29; H, 4.22; N, 3.09. Found: C, 50.66; H, 4.44; N, 3.32.

N-(4-Methoxyphenyl)-2-[4,5-bis(ethylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-c]pyrrole (3c). This compound was obtained from the reaction with 11c as yellow solid, yield 129 mg (27%); mp 175-176.5 °C (from dichloromethane dichloromethane-petroleum ether (60-90 °C)); IR (KBr): ν 1633, 1518, 1248 cm⁻¹; ¹H NMR (CDCl₃): δ 1.34 (3H, t, J = 7.4 Hz, CH₃), 2.88 (2H, q, J = 7.4 Hz, CH₂), 3.85 (3H, s, OCH₃), 6.81 (2H, s, 4-6-H), 6.95 (2H, d, J = 8.9 Hz, 3'-5'-H), 7.25 (2H, d, J = 8.9 Hz, 2'-6'-H); MS (APCI): m/z 470 ([M+1]). Anal. Calcd for C₁₉H₁₅N₂S₆: C, 48.58; H, 4.08; N, 2.98. Found: C, 48.06; H, 4.14; N, 3.00.

N-(4-Chlorophenyl)-2-[4,5-bis(ethylthio)-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-c]pyrrole (3d). This compound was obtained from the reaction with 11d as yellow solid, yield 36 mg (8%); mp 222-223 °C (from dichloromethane); IR (KBr): ν 1624, 1510, 1316 cm⁻¹; ¹H NMR (CDCl₃): δ 1.34 (3H, t, J = 7.4 Hz, CH₃), 2.88 (2H, q, J = 7.4 Hz, CH₂), 6.86 (2H, s, 4-6-H), 7.26 (2H, d, J = 8.9 Hz, 3'-5'-H), 7.40 (2H, d, J = 8.9 Hz, 2'-6'-H); MS (APCI): m/z 474 ([M+1]). Anal. Calcd for C₁₉H₁₅N₂S₆: C, 45.59; H, 3.40; N, 2.95. Found: C, 45.66; H, 3.41; N, 2.80.

REFERENCES