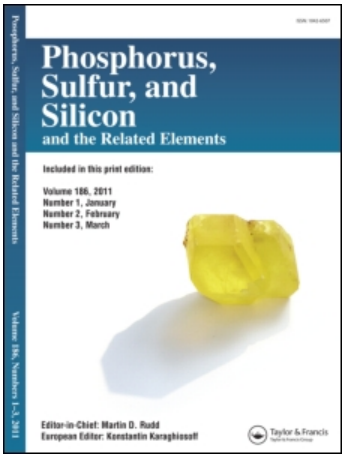

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Thiafulvenes and Thiafulvalenes in Organic Chemistry: Synthesis and Study its Behavior towards Some Chemical Reagents

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Trithiafulvenes were prepared through cycloaddition of 3-thioxo-1,2-dithioles to several electrophilic alkenes and alkynes. Treatments of the product with phenylhydrazine and malononitrile afforded the hydrazone and the dinitrilene derivatives respectively. The bromination and subsequent treatment with KCN and malononitrile afforded the diene derivative. The aniline derivative was also obtained by treatment with chloroaniline.

Keywords Sulfur heterocycles; tetrathiafulvalenes; thiafulvalenes; trithiafulvenes

INTRODUCTION

Trithiafulvenes and tetrathiafulvalenes were found to possess wide applications in the fields of organic metals and superconductors,[1] supramolecular chemistry,[2] molecular scale electronic and optical components,[3] biological activities,[4] reaction catalysis,[5] and as diagnostic and therapeutic agents[6] and sensors.[7]

Owing to the foregoing knowledges, the authors tried to synthesize some new heterocyclic compounds in the hope of obtaining some antimicrobial agents. The prepared compounds were examined to stop or at least delate the growth of the harmful microorganisms that infect

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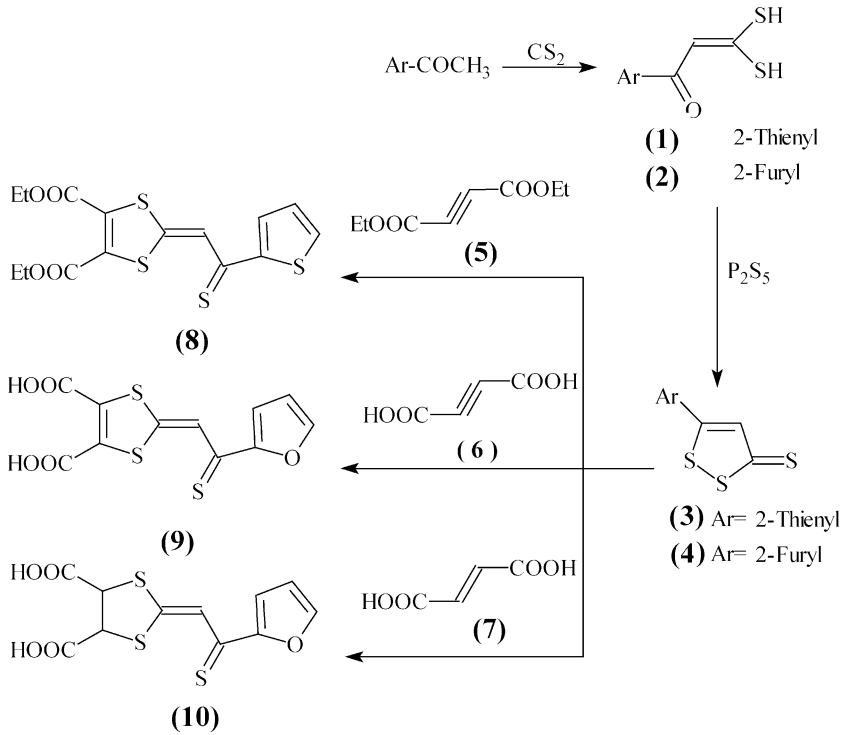
sugar industry and cause damages to sucrose molecule and great loss in sugar production.

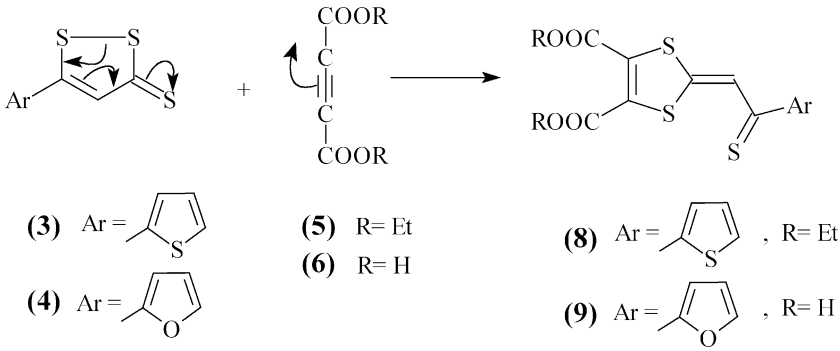
Starting with α-oxoketen-gemdithioles (1) and (2), the trithiones (3) and (4) could be prepared through sulfurization of (1) and (2) with phosphorous pentasulfide.[8–10] The common key step for the synthesis of 1,3-dithiole-2-ylidenes (8,9) and 1,3-dithiolane-2-ylidene (10) is the Diel's-Alder cycloaddition of 3-thioxo-1,2-dithioles (3) and (4) to an electrophilic alkynes,[11] e.g., diethylacetylenedi-carboxylate (5) and acetylenedicarboxyolic acid (6) or alkenes,[12] e.g., maleic acid (7) in methylene chloride (Scheme 1).



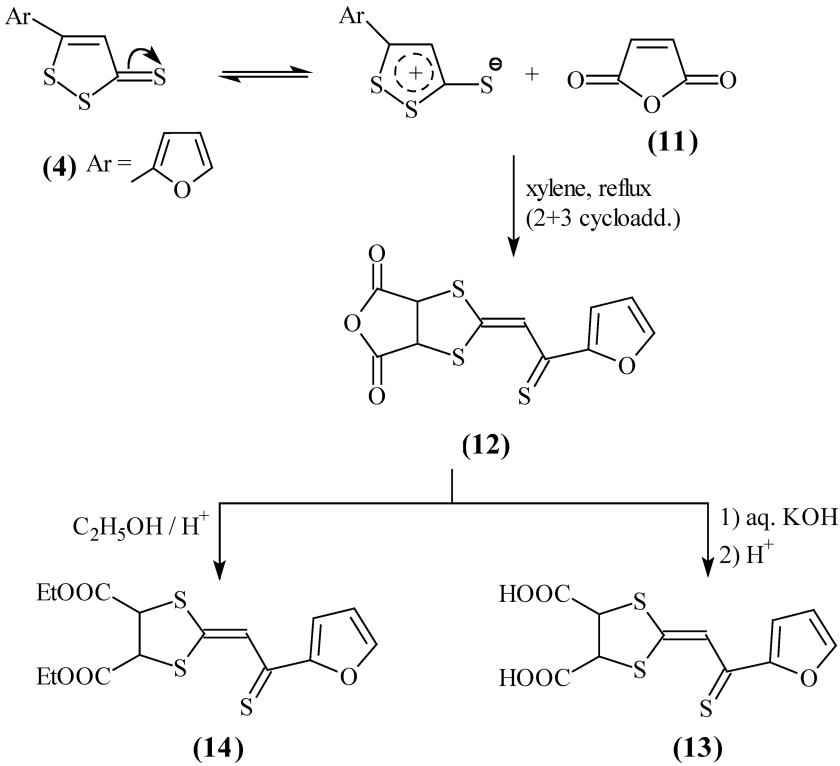
SCHEME 1

Formation of the products (8–9) is suggested to proceed as follows:

Structure of the product (10) was confirmed chemically via reacting (4) with maleic anhydride (11) in boiling xylene followed by alkaline hydrolysis and acidification of the product (12) to give the diacid derivative (13), which was found to be identical with (10). Furthermore, boiling the anhydride (12) in ethanol containing few drops of sulfuric acid resulted in anhydride ring opening and the diester derivative (14) was formed.



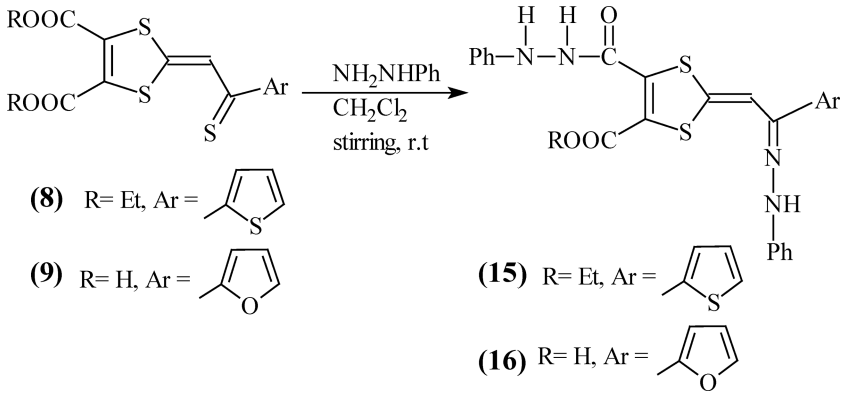
Formation of the anhydride (12) was assumed to proceed via 1,3-dipolar cycloaddition reaction (Scheme 2).



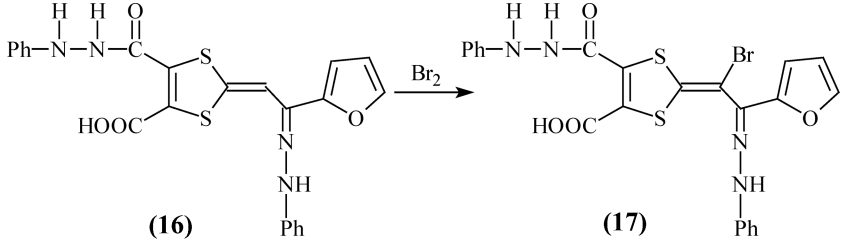
SCHEME 2

Trithiafulvenes (8) and (9) when allowed to react with phenylhydrazine (2 mole) in methylene chloride gave a title compounds of the

types (15) and (16). ^{1}HNMR spectra for (15 and 16) indicates the presence of both [CO–NH–NH–Ph] and C=N–NH–Ph moieties, while the peak for thione group disappeared.



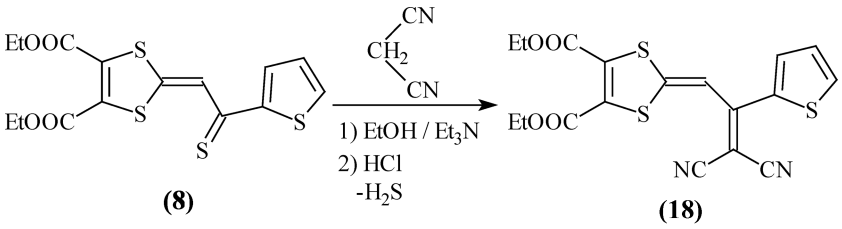
1,3-Dithiole-2-ylidene is a strong donor group,[13] so, the hydrogen atom attached at C2 is available for replacement. As a result, bromination of (16) proceeded smoothly yielding the bromo-derivative (17).

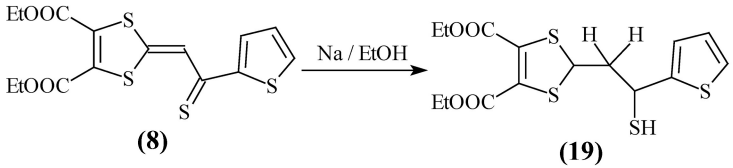


Furthermore, reaction of trithiafulvene (8) with malononitrile resulted in the formation of product (18). Malononitrile was added to the thione group instead of ethylenic double bond and finally hydrogen sulfide was detected. Spectral measurements proved the presence of proton located at C2 and IR spectra shows a peak corresponding to cyano groups.

Addition reaction to trithiafulvene (8) was investigated. On reduction of (8) with Na/EtOH, the reduced product (19) was obtained. Formation of (19) was confirmed by ^{1}HNMR spectra where a newly methylene and thiole protons were detected.

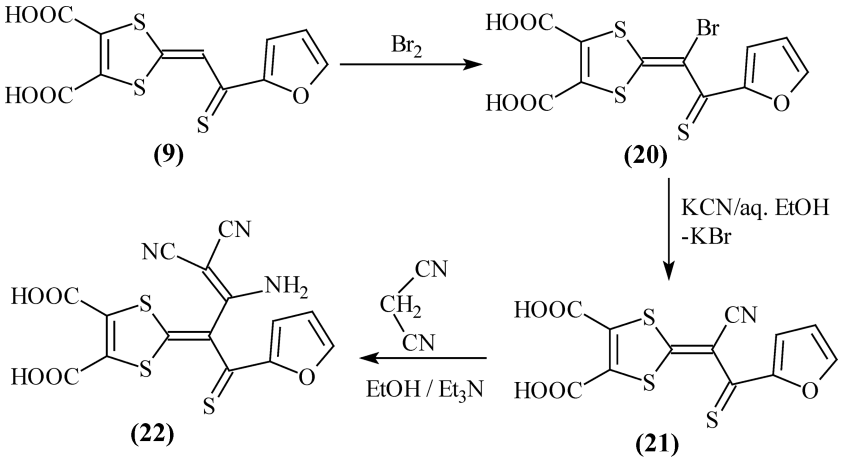
Moreover, treatment of the substrate (9) with bromine formed the substitution reaction product (20). Structure of (20) was proved via the





disappearance of the signal characteristic of the proton at C2. Stirring the product (20) with potassium cyanide in aqueous ethanol favored substitution of bromine atom by cyanide moiety and finally the product (21) was gathered (Scheme 3).

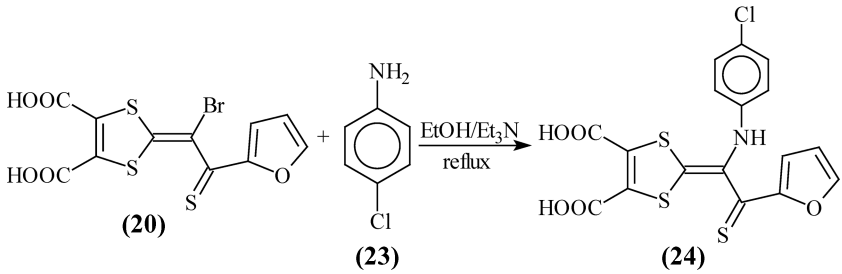
Consequently, by treating the diacid trithiafulvene derivative (21) with malononitrile in boiling absolute ethanol in presence of triethylamine, the reaction takes place towards addition to cyano group forming a dieno-structure (22) (Scheme 3).



SCHEME 3

The reaction of substrate (20) with aromatic amines, e.g., p-chloroaniline (23) in boiling ethanol containing catalytic amount of

triethylamine, led to the formation of product (24) via a debromination addition reaction. The structure of (24) was proved by spectral and analytical measurements.



EXPERIMENTAL SECTION

Elemental analysis: were carried out at Microanalytical Unit, Cairo University Mass spectra: were obtained on a GCMS-QP 1000 EX mass Spectrometer with ionization potential of 70 eV and a Mass Spectrometer MS 30 MS9 (AEI) at 70 eV. IR spectra: were determined with a Shimadzu IR 408 Infrared Spectrophotometer using KBr wafer technique. ^{1}H-NMR: carried out on Varian EM 390 (300 MHz) using TMS as internal standard and chemical shifts are expressed as ppm (δ). Melting points: All melting points are uncorrected and were determined either on a sulfuric acid apparatus or on a Kofler melting point apparatus.

Synthesis of Dithioles (1) and (2)—General Procedure

Carbondisulfide (0.60 ml; 0.01 mol) was added to (0.01 mol) acetylthiophene or acetylfuran in dry benzene (150 ml) and the mixture was cooled to 0–5°C. Potassium tertiary butoxide (2.8 g; 0.025 mol) was added gradually to the cooled mixture with continuous shaking. Cold water was then added with continuous shaking and the benzene layer was separated. The aqueous layer was washed several times with petroleum ether 40/60. The aqueous layer was cooled and gradually acidified with concentrated sulfuric acid. The separated precipitate was filtered off and recrystallized from benzene to give:

1) thiole (1) from acetylthiophene as red crystals, m.p. 83°C.(yield 89.21%) Elemental analysis: $C_7H_6OS_3$, M.wt 202.298 Calc.:C 41.56,H 2.99,S 47.54 Found:C 41.60,H 3.0, S 47.56; and

2) thiole (2) from acetylfuran as yellowish-brown crystals, m.p. 50°C. (yield 78.93%). Elemental analysis: $C_7H_6O_2S_2$, M.wt 186.238 Calc.:C 45.14,H 3.25,S 34.43 Found:C 45.11,H 3.25,S 34.40.

Synthesis of 1,2-dithiacyclopentene-3-thiones (3) and (4)—General Procedure

To the dithiole 1 or 2 (0.01 mol) in dry benzene (100 ml) was added phosphorouspentasulfide (0.15 mol). The reaction mixture was heated on a water bath for 5 h, and then filtered while hot. The clear benzene layer was concentrated to its half volume followed by addition of appropriate quantity of petroleum ether 40/60. The precipitated solid product was filtered off and washed twice with petroleum ether 40/60 giving the required thione (3) or (4).

1) Dithiole (1) gave 1,2-dithiole-3-thione (3) as reddish-brown crystals from methylene chloride, m.p. 118°C, (yield 78.74%). Elemental analysis: $C_7H_4S_4$, M.wt 216.342 Calc.:C 38.86,H 1.86,S 59.28 Found:,C 39.01,H 1.82,S 60.02
2) Dithiole (2) gave 1,2-dithiole-3-thione (4) as brown crystals from methylene chloride, m.p. 110°C, (yield 86.34%). Elemental analysis: $C_7H_4OS_3$,M.wt 200.282 Calc.:C 41.98, H 2.01,S 48.02 Found:C 42.01,H 2.00,S 48.03

Synthesis of 1,3-Dithiole-2-ylidene Systems (8), (9) and (10)

Diethyl-2-(2-Thien-2-yl-2-thioxoethylidene)-1,3-dithiole-4,5-dicarboxylate (8)

A mixture of dithiolethione 3 (2.16 g; 0.01 mol) and diethylacetylenedicarboxylate 5 (1.5 ml; 0.01 mol) was stirred in methylene chloride (30 ml) at room temperature for 3 h. The solvent was left to evaporate at room temperature, and the formed precipitate was recrystallized from diethylether as violet crystals, m.p. 105°C in quantitative yield (89.63%). Elemental analysis: $C_{15}H_{14}O_4S_4$, M.wt 386.502 Calc.:C 46.61,H 3.65,S 33.18 Found:C 46.66,H 3.66, S 33.08.

2-[2-(2-Furyl)-2-thioxoethylidene]-1,3-dithiole-4,5-dicarboxylic Acid (9)

A mixture of dithiolethione 4 (2.0 g; 0.01 mol) and acetylenedicarboxylic acid 6 (1.14 ml; 0.01 mol) was stirred in methylene chloride (30 ml) at room temperature for 3 h. The solvent was left to evaporate at room temperature and the formed precipitate was gathered

and recrystallized from ethanol as dark brown crystals, m.p. 165°C, (yield 92.62%). Elemental analysis: $C_{11}H_6O_5S_3$,M.wt 314.338 Calc.:C 42.03,H 1.92, S 30.60 Found:C 42.15,H 1.89,S 30.52 IR (KBr): ν (cm^{-1}): 1720 (—C=O), 1170 (—C=S), 2700 (—OH) of carboxyl, 1480 (>C=CH).

2-[2-(2-Furyl)-2-thioxoethylidene]-1,3-dithiolane-4,5-dicarboxylic Acid (10)

A mixture of dithiolethione 4 (2.0 g; 0.01 mol) and maleic acid 7 (1.16 ml; 0.01 mol) was stirred in methylene chloride (20 ml) at room temperature for 2 h. The solvent was left to evaporate at room temperature and the product was collected and recrystallized from dioxane as reddish-brown crystals, m.p. 240°C in quantitative yield (93.21%). Elemental analysis: $C_{11}H_8O_5S_3$, M.wt 316.354 Calc.: C 41.76,H 2.55, S 30.40 Found:C 41.87,H 2.52,S 30.35 IR (KBr): ν (cm^{-1}): 1720 (—C=O), 1170 (—C=S), 2700 (—OH) of carboxyl, 1480 (>C=CH). ^{1}H-NMR (DMSO): δ (ppm): 7.46–7.78 (m, 3H, furan), 8.04 (s, 1H, C=CH), 6.64-6.84 (s, 2H, C4-C5-1,3-dithole).

Synthesis of 2-[2-(2-Furyl)-2-thioxoethylidene]dihydro[1,3]dithiolo[4,5-c]furan-4,5-dione (12)

Dithiolethione 4 (2.0 g; 0.01 mol) was refluxed with maleic anhydride 11 (0.98 g; 0.01 mol) in xylene (15 ml) for 2 h. The reaction mixture was concentrated, cooled and the formed precipitate was filtered off and recrystallized from ethanol as deep violet crystals, m.p. 180°C in quantitative yield, (88.95%). Elemental analysis: $C_{11}H_6O_4S_3$, M.wt 298.338 Calc.:C 44.28,H 2.03,S 32.24 Found:C 44.43,H 2.04,S 32.33.IR (KBr): ν (cm^{-1}): 1090 (—C=S), 1480 (C=CH). ^{1}H-NMR (DMSO): δ (ppm): 7.34–7.69 (m, 3H, furan), 8.34 (s, 1H, C=CH), 6.62–6.64 (s, 1H, C4), 6.25–6.28 (s, 1H, C5, C4-C5-1,3-dithiole).

Synthesis of 2-[2-(2-Furyl)-2-thioxoethylidene]-1,3-dithiolane-4,5-dicarboxylic Acid (13)

The anhydride derivative 12 (2.98 g; 0.01 mol) was stirred with hot aqueous potassium hydroxide (2 g KOH/25 ml H_2O) for 1 h. The reaction mixture was acidified with concentrated hydrochloric acid and the formed precipitate was filtered off and recrystallized from dioxane as brown crystals, m.p. 240°C, (yield 71.26%). Elemental analysis: $C_{11}H_8O_5S_3$, M.wt 316.354 Calc.: C 41.76, H 2.55, S 30.40; Found: C 41.86,H 2.00,S 30.37. IR (KBr): ν (cm^{-1}): 1720 (—C=O), 1170 (—C=S), 2700 (—OH) of carboxyl, 1480 (>C=CH). ^{1}H-NMR (DMSO): δ (ppm): 7.46-7.78 (m, 3H, furan), 8.04 (s, 1H, C=CH), 6.64-6.84 (s, 2H, C4-C5-1,3-dithiole).

Synthesis of Diethyl 2-[2-(2-Furyl)-2-thioxoethylidene]-1,3-dithiolane-4,5-dicarboxylate (14)

The anhydride 12 (2.98 g; 0.01 mol) was boiled in ethanol (25 ml) containing sulfuric acid (1 ml) for 5 h. The diester derivative (14) was obtained after neutralization with alkali. The separated solid product was filtered off and recrsytallized from ethanol as orange crystals, m.p. 150°C, (yield 69.22%). Elemental analysis: $C_{15}H_{16}O_5S_3$, M.wt 372.458 Calc.:C 48.37,H 4.33, S 25.82 Found: C 48.52,H 4.32, S 25.88 IR (KBr): ν (cm^{-1}): 1540 (—COO^-), 1050 (C=S), 1490 (—CH_2), 1410, 1380 (—CH_3). ^{1}H-NMR (DMSO): δ (ppm): 8.1–8.11 (s, 1H, C=CH), 1.24 (t, 6H, $2CH_3$ ester), 3.35 (s, 4H, $2CH_2$ ester), 6.83-6.85 (s, 2H, C4-C5 cyclic, 1,3-dithiacyclopent.), 7.58-7.71 (m, 3H, furan).

5-(N-Phenylhydrazinocarbonyl)-2-(2-phenylhydrazino)-2-thiophene-2-yl-ethylidene-1,3-dithiole (15)

Obtained from (8) as a pale yellow crystals from methylene chloride, m.p. 240°C, (yield 60.37%.) Elemental analysis: $C_{25}H_{22}N_4O_3S_3$,M.wt 522.638 Calc.:C 57.45, H 4.24, N 10.72, S 18.40 Found:C 57.49,H 4.18,N 10.75, S 18.38 IR (KBr): ν (cm^{-1}): 1730 (C=O), 3000 (—CH), 1640 (—CONH), 1490 (—CH_2), 1390 (—CH_3), 750 (5H adj.). ^{1}H-NMR (DMSO): δ (ppm): 8.3 (s, 1H, C=CH), 6.75–7.04 (m, 10H, $2C_6H_5$), 7.6 (s, 1H, N—NH), 7.12–7.22 (m, 3H, thiophene), 8.1 (s, 1H, CONH), 7.32 (q, 2H, CH_2), 7.43 (s, 3H, CH_3).

(2E)-2-[2-(2-Furyl)-2-(2-phenylhydrazino]-N-phenyl-1,3-dithiole-4-carboxylic Acid-3-carbohydrazide (16)

Obtained from (9) as a brownish-orange crystals from dioxane, m.p. 80°C, (yield 60.81%). Elemental analysis: $C_{23}H_{18}N_4O_4S_2$,M.wt 478.526 Calc.:C 57.73,H 3.79,N 11.71,S 13.40 Found:,C 57.76,H 3.77,N 11.73 S 13.37 IR (KBr): ν (cm^{-1}): 1715 (C=O), 750 (5H, adj), 2700 (—OH) of carboxyl, 1640 (—CONH).

Synthesis of (2E)-2-[1-bromo-2-(-2-furyl)-2-phenylhydrazino]-1,3-dithiole-4-carboxylic acid-3-carbohydrazide (17)

A mixture of 16 (4.78 g; 0.01 mol) in chloroform (20 ml) and bromine (0.96 ml; 0.01 mol) in chloroform (10 ml) was stirred in direct sunlight for 2 h. The solvent was left to evaporate at room temperature and the product was collected and recrystallized from methylene chloride as dark brown crystals, m.p. 205°C, (yield 82.81%). Elemental analysis: $C_{23}H_{17}BrN_4O_4S_2$, M.wt 557.43 Calc.:C 49.55 H 3.07, N 10.05, S 11.50 Found:C 49.74 H 3.05, N 10.09, S 11.49

Synthesis of Diethyl-2-(3,3-Dicyano-2-thien-2-yl-prop-2-enylidene-1,3-dithiole-4,5-dicarboxylate (18)

A mixture of trithiafulvene 8 (3.86 g; 0.01 mol) and malononitrile (0.78 ml; 0.01 mol) was heated under reflux in absolute ethanol (30 ml) for 3 h in the presence of few drops of triethylamine. The reaction mixture was concentrated, cooled and acidified with dilute hydrochloric acid. The formed precipitate was filtered off and recrystallized from ethanol as brown crystals in quantitative (yield (96.11%), m.p. 150°C. Elemental analysis: $C_{18}H_{14}N_2O_4S_3$, M.wt 418.488 Calc.: C 51.66, H 3.37,N 6.69,S 22.98 Found:C 51.95,H 3.38,N 6.74, S 22.95 IR (KBr): ν (cm^{-1}): 1540 (—COO^-), 1735 (—C=O), 2500 (—CN), 1650 (—C=C—). ^{1}H-NMR (DMSO): δ (ppm): 1.23 (t, $2CH_3$), 3.89-3.98 (q, $2CH_2$), 7.22-7.95 (m, 3H, thiophene), 8.15 (s, 1H, C=CH).

Synthesis of Diethyl 2-(2-mercapto-2-thien-2-yl-ethyl)-1,3-dithiole-4,5-dicarboxylate (19)

Small pieces of sodium metal (0.03 mol) were added gradually while stirring at room temperature to trithiafulvene (8) (0.01 mol, 3.865 g) in absolute ethanol (20 ml). The formed brown precipitate was filtered off and recrsytallized from ethanol, m.p. 220°C, (yield 77.13%). Elemental analysis:$C_{15}H_{18}O_4S_4$ M.wt 390.534 Calc.:C 46.13,H 4.65,S 32.84 Found:C 46.09, H 4.60,S 32.84 IR (KBr): ν (cm^{-1}): 1355 (—COO—), 1475 (—CH_2), 2850 (—SH), 1735 (—C=O). ^{1}H-NMR (DMSO): δ (ppm): 1.23 (t, 3H, ester), 2.51-2.52 (s, —CH_2-), 8.1 (s, 1H, —CH), 7.18–7.84 (m, 3H, thiophene), 3.65 (q, —CH_2-ester), 8.71 (s, 1H, —CH—CH_2), 1.44 (s,1H SH).

Synthesis of 2-[1-Bromo-2-(2-furyl)-2-thioxoethylidene]-1,3-dithiole-4,5-dicarboxylic Acid (20)

A mixture of trithiafulvene 9 (3.14 g; 0.01 mol) in chloroform (20 ml) ,and bromine (0.96 ml; 0.01 mol) in chloroform (10 ml) was stirred in direct sunlight for 2 h. The solvent was left to evaporate at room temperature. Product (20) was collected and recrsytallized from methanol in the form of light brown crsytals, shrinking at 145°C, (yield 80.42%) . Elemental analysis: $C_{11}H_5BrO_5S_3$, M.wt 393.246. Calc.:C 33.59,H 1.28,Br 20.32,S 24.46 Found:C 33.92,H 1.30, Br 21.00, S 24.47 IR (KBr): ν (cm^{-1}): 2700 (—OH) of carboxyl, 1200 (—C=S), 1720 (—C=O)

Synthesis of 2-[1-Cyano-2-(2-furyl)-2-thioxoethylidene]-1,3-dithiole-4,5-dicarboxylic Acid (21)

To the bromo derivative 20 (3.93 g; 0.01 mol) in ethanol (20 ml), aqueous potassium cyanide (0.65 g; 0.01 mol) was added. The mixture was stirred at room temperature for 3 h. After cooling, the solid product so formed was collected and recrystallized from dioxane to give a dark brown crystals, m.p. >250°C, (yield 30.37%). Elemental analysis: $C_{12}H_5NO_5S_3$, M/wt 339.348. Calc.: C 42.47, H 1.49, N 4.13, S 28.34 Found:C 42.47, H 1.47, N 4.09, S 28.38. IR (KBr): ν (cm^{-1}): 2800 (—OH) of carboxyl, 2100 (—CN), 1710 (—C=O), 1120 (—C=S), 1600 (C=C).

Synthesis of 2-[2-Amino-3,3-dicyano-1-(2-furylcarbonothioyl)prop-2-enylidene]-1,3-dithiole-4,5-dicarboxylic Acid (22)

A mixture of the cyano derivatives 21 (4.19 g; 0.01 mol) and malnonitrile (0.78 g; 0.01 mol) in ethanol (30 ml) containing catalytic amount of triethylamine (0.3 ml) was refluxed for 4 h. The solvent was concentrated and the remaining was cooled. The formed precipitate was filtered off and recrystallized from dioxane, m.p. >250°C, yield 80%. Elemental analysis: $C_{15}H_7N_3O_5S_3$, M/wt 405.41. Calc.: C 44.44, H 1.74, N 10.37, S 23.72 Found:C 44.49,H 1.75,N 10.35, S 23.68 IR (KBr): ν (cm^{-1}): 2210 (-CN), 1710 (—C=O), 3335 (—NH_2), 2800 (—OH) of carboxyl, 1020 (C=S), 1650 (—C=C—).

Synthesis of 1-[(4-Chlorophenyl)amino]-2-(2-furyl)-2-thioxoethylidene]-1,3-dithiole-4,5-dicarboxylic Acid (24)

A mixture of the bromo derivative 20 (3.93 g; 0.01 mol) and p-chloroaniline 23 (1.27 g; 0.01 mol) in ethanol (50 ml) containing catalytic amount of triethylamine (0.3 ml) was refluxed for 5 h. The reaction mixture was concentrated, cooled and the formed precipitate was filtered off, washed with water and recrsytallized from dioxane as deep green crystals, m.p. 220°C, (yield 60.27%%). Elemental analysis: $C_{17}H_{10}ClNO_5S_3$, M/wt 439.895 Calc.: C 46.41, H 2.29. N 3.18, S 21.86 Found:C 46.45, H 2.28,N 3.18, S 21.83.

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