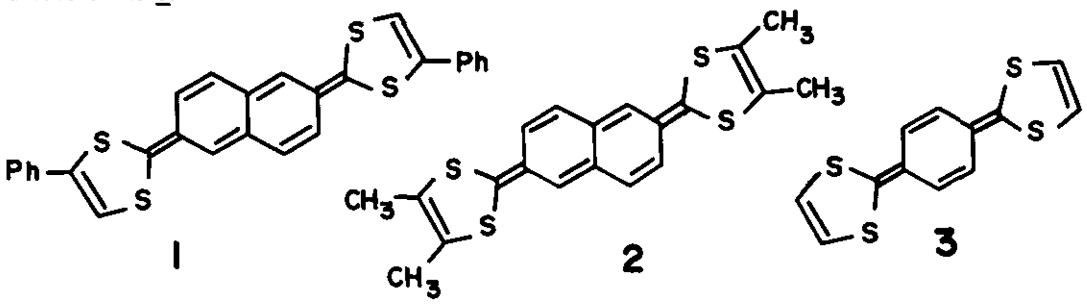
ORGANIC CONDUCTORS: SYNTHESIS AND COMPLEX FORMATION OF SUBSTITUTED 2,2'-(2,6-NAPHTHALENE)BIS[1,3-DITHIOLIUM] SALTS

Shuh-Chung Chen and Eugene LeGoff*
Department of Chemistry
Michigan State University
East Lansing, Michigan 48824, USA

Abstract—The synthesis and reactions the bis(dithiolium) salts 7 and 8 are described. Conversion to iodine and TCNQ complexes were investigated.

As a contribution to the understanding of metallic-like conductivity in donor-acceptor systems (so called "organic metals")[1], we have undertaken the synthesis of two naphthalene-inserted tetrathiafulvalene donors, 1 and 2, which have structures analogous to the electron donors tetrathiafulvalene and 3.[2,3]

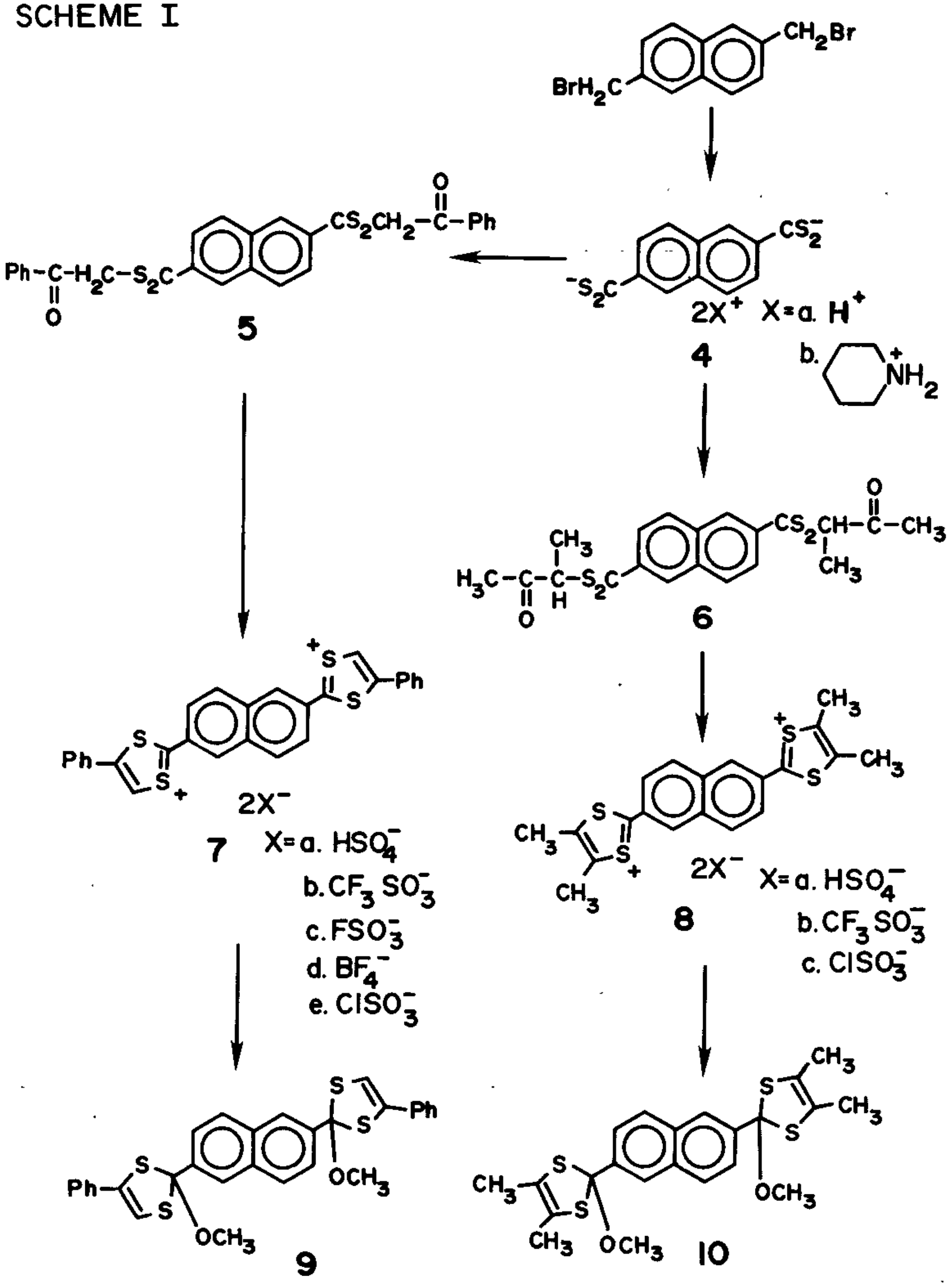


1 2 3

The synthesis of the precursors of 1 and 2 is outlined in Scheme I. The unknown piperdinium salt of 2,6-naphthalenedicarbodithioic acid 4b was prepared in 58% yield from the reaction of 2,6-bis(bromomethyl)naphthalene with sulfur and sodium methoxide (method of Ueno[2], Farbre[3] and Becke[4]). The free acid 4a was unstable. Reaction of the salt 4b with either phenacyl bromide or 3-chlorobutanone gave the dithioester 5 (87% yield) and 6 (30% yield) respectively. The bis-cyclization reaction, carried out by dissolving the dithioesters in cold concentrated acid (H_2SO_4, CF_3, FSO_3H or $ClSO_3H$), gave the orange bis-dithiolium salts 7 and 8 (Table I). The fluoroborate salt 7d was prepared by heating the dithioester 5 with phosphorus pentasulfide and fluoroboric acid (method of Takamizawa and Hirai[4]). The trifluomethanesulfonate 7b was isolated as the monohydrate while the bisulfate salt 8a was complexed with one equivalent of sulfuric acid.

The structures of 7 and 8 were substantiated by spectral data. The characteristic C═O and C═S bands in the infrared were absent. The NMR spectra of 7 have, in addition to the central aromatic hydrogens (6H) at δ 8.2-8.4 ppm, a singlet for the 1,3-dithiolium ring hydrogens (2H) at δ 8.8

SCHEME I



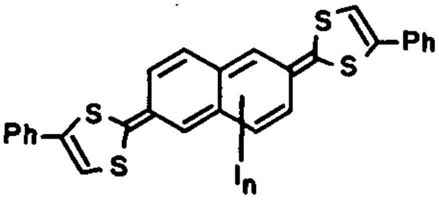
CH2Br
BrH2C
CS2CH2–C(=O)–Ph
Ph–C(=O)–H2C–S2C
5
CS2−
−S2C
2X+ X= a. H+
b. piperidinium (NH2+)
4
CS2CH(CH3)–C(=O)–CH3
H3C–C(=O)–C(CH3)H–S2C
6
Ph
S+
S
7
2X−
X= a. HSO4−
b. CF3SO3−
c. FSO3−
d. BF4−
e. ClSO3−
CH3
8
2X−
X= a. HSO4−
b. CF3SO3−
c. ClSO3−
OCH3
9
10

dithiolium salt	7		8	
	mp	yield	mp	yield
a) HSO_4^-	246-249° (d)	85%	>350°	73%
b) $CF_3SO_3^-$	227-230° (d)	95%	313-314° (d)	62%
c) FSO_3^-	256-257° (d)	90%	----	---
d) BF_4^-	249-252° (d)	86%	----	---
e) $ClSO_3^-$	268-270° (d)	73%	>320°	38%

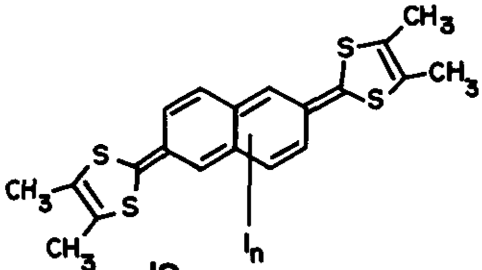
ppm and a multiplet of aromatic hydrogens (10H) centered at 7.8 ppm. The spectra of 8 have 12 methyl hydrogens at δ 2.82 ppm and 6 aromatic hydrogens at 8.0-8.6 ppm. Sodium methoxide converts 7 and 8 to the dimethoxy derivatives 9 and 10 in near quantitative yield. Reaction of 9 or 10 with concentrated acid gives back the corresponding salt 7 or 8.

The reduction of the dication 7 with lithium iodide or tetrabutylammonium iodide proceeded cleanly to give a black, microcrystalline iodine complex 11 (80% yield). Elemental analysis of 11 indicates that it is a non-stoichiometric compound having a cation to iodine ratio of 25:49. The long wavelength absorption of this complex at 675 nm, a bathochromic shift of 210 nm from the dication 7, is the result of a highly delocalized, conjugated system. The dithiolium salt 7 was recovered from the complex 11 upon treatment with excess concentrated acid. The formation of 11 is probably the result of electron transfer from iodide to the dication 7 followed by iodine-iodide aggregation to form a non-stoichiometric, complex radical cationic salt.

In contrast to 7, the dithiolium salt 8 did not form an iodine complex when treated with tetrabutylammonium iodide. However, when 10 was treated with hydriodic acid, a black solid was formed which appeared to be an impure sample of complex 12. The dithiolium salts 8 can be regenerated from 12 by treatment with concentrated acid.



11



12

Reaction of the bis(dithiolium) salt 7b with two equivalents of Li^{+} $TCNQ^{\dot{-}}$ in acetonitrile affords a dark green solution which displayed uv-visible absorption bands characteristic of neutral tetracyano-p-quinodimethane (TCNQ) and the radical anion $TCNQ^{\dot{-}}$. Thus, it appears that in solution, a mix-valence complex salt has been formed. Thus far, suitable conditions have not been found which would yield a crystalline complex.

EXPERIMENTAL SECTION

Dipiperidium 2,6-Naphalenedicarbodithioate (4b). A solution of sodium methoxide (80 mM), and sulfur (2.56g, 80 mM) in 60 mL of dry methanol was refluxed for 2 h. To this refluxing solution was added 2,6-bis(bromomethyl)naphthalene (5.8g, 18.5 mM) over 1 h. This solution was refluxed for 7 h, cooled and the solvent evaporated *in vacuo*. The residue was dissolved in a minimum amount of water and filtered. The deep violet filtrate was acidified with 10% HCl to give a green precipitate of 4a. This precipitate was dissolved in chloroform (1.5 L) to which was quickly added piperidine (3.5g, 35 mM). The resulting solution was taken to near dryness *in vacuo*. Filtration afforded the olive-green product 4b (4.8g, 58% yield), mp 154-156°C; IR(Nujol):1000cm^{-1} (S=C-S).

Diphenacyl 2,6-Naphthalenedicarbodithioate (5). To a stirred suspension of the dipiperidinium salt 4b (0.45g, 1 mM) in 100 mL of methylene chloride was added dropwise a solution of phenacyl bromide (0.398g, 2 mM) in 25 mL of methylene chloride at room temperature. After stirring for 4 h, the solvent was removed *in vacuo*. The residue was crystallized from chloroform/hexane to yield red crystals of 5 (0.45g, 87% yield), mp 198-199°C; IR (Nujol) 1690cm^{-1} (C=O, 1205 (C=S), 1050, 880; Calcd. for $C_{28}H_{20}O_2S_4$: C, 65.08; H, 3.90. Found: C, 64.93; H, 3.86%.

Bis(1-methyl-2-oxopropyl)-2,6-naphthalenedicarbodithioate (6). To a stirred suspension of 4b (0.45g, 1 mM) in 100 mL of dry ethanol was added 3-chloro-2-butanone (0.21g, 2 mM) in 10 mL of ethanol. The brown suspension dissolved with spontaneous formation of orange crystals. After stirring for 1 h at room temperature, the solvent was removed *in vacuo* and the residue crystallized from chloroform to give red crystals of 6 (0.03g, 30% yield), mp 180-181°C; IR (Nujol) 1700cm^{-1} (C=O), 1325, 1220 (C=S), 1175, 1150, 1130, 1045, 925, 880, 815, 800; UV ($CHCl_3$) λ_{max}: 345, 505 nm; PMR ($CDCl_3$): δ ppm 1.65 (d, 6H), 2.4 (s, 6H), 4.9 (q, 2H) and 7.6-8.4 (m, 6H); Calcd. for $C_{20}H_{20}O_2S_4$: C, 57.11; 4.79. Found: C, 57.14; H, 4.93%.

2,6-Naphthalene-bis(4-phenyl-1,3-dithiolium) Trifluoromethanesulfonate (7b). Phenacyl 2,6-naphthalenedicarbodithioate (5), (0.1g, 0.2 mM) was carefully dissolved in 10 mL of cold trifluoroacetic acid. The cold solution was poured into 50 mL of ethyl acetate to give, after washing with ethyl acetate, the bis-trifluoromethanesulfonate salt 7b (0.11g, 85% yield) mp 246-249°C (dec); PMR (CF_3COOH): δ ppm 8.8 (s, 2H), 8.1-8.8 (m, 6H); UV (CH_3CN) λ_{max}: 465, 340, 250, 225 nm; Calcd. for $C_{30}H_{18}F_6O_6S_6 \cdot H_2O$: C, 45.10; 2.52. Found: C, 45.08; H, 2.62%.

fonate 7c and chlorosulfonate 7e salts were prepared by the same procedure.

2,6-Naphthalene-bis(4-phenyl-1,3-dithiolium) Fluoroborate (7d). Phenacyl ester 5 (1.2g, 2.3 mMl), 0.95 mL of fluoroboric acid (48% aqueous solution) and P_2S_5 (0.6g, 2.7 mM) were refluxed in 14 mL of glacial acetic acid for 20 h. An orange suspension was obtained at the end of the heating period. The solvent was removed in vacuo and the residue was washed with 50 mL of ethanol to yield 7d (1.3g, 85% yield), mp 249-252°C (dec).

2,6-Nathalene-bis(4,5-dimethyl-1,3-dithiolium) Bisulfate (8a). Carefully, the ester 6 (0.1g) was dissolved in 10 mL of cold concentrated sulfuric acid. The resulting solution was poured in 150 mL of ethyl acetate with stirring to precipitate the salt 8a (0.11g, 73% yield), mp > 350°C; PMR (CF_3COOH): δ ppm 2.82 (s, 12H), 8.0-8.6 (m, 6H); UV (CH_3CN) λ_{max}: 442 nm; Calcd. for $C_{20}H_{20}O_8S_8 \cdot H_2SO_4$: C, 35.39; H, 3.27. Found: C, 35.32, H, 3.51%. The trifluoromethanesulfonate 8b and chlorosulfonate 8e salts were similarly prepared.

Reaction of 7b with Sodium Methoxide. To a solution of the trifluoromethanesulfonate salt 7b (0.1g, 0.13 mM) in dry methanol was added a solution of sodium methoxide (0.26 mM) in methanol. The orange color of the original solution faded away immediately. After stirring at room temperature for 1 h, the solvent was removed in vacuo. The white solid obtained was collected, washed with methanol and dried to give the dimethoxy derivative 9 (0.05g, 72% yield), mp 175-180°C; IR (Nujol) 1550, 1165, 1130, 1080, 730cm^{-1}; PMR ($CDCl_3$): δ ppm 3.5 (s, 6H), 6.4 (s, 2H), 7.1-7.5 (m, 10H), 7.6-8.3 (m, 6H). Mass spectrum m/e: 544 (parent), 513, 482, 379, 304, 241, 149, 134, 121, 57.40. Calcd. for $C_{30}H_{24}O_2S_4$: C, 66.14; H, 4.44. Found: C, 65.83; H, 4.61%.

Reaction of salt 8b with sodium methoxide. The procedure described above for salt 7b was followed. The yield of the dimethoxy derivative 10 was quantitative; mp > 350°C; PMR ($CDCl_3$): δ ppm 1.95 (s, 12H), 3.47 (s, 6H), 7.67-8.17 (m, 6H).

Reaction of 10 with HI. To a suspension of 10 (0.45g, 1 mM) in 10 mL of water was added 15 mL of 48% aqueous HI. The resulting brown suspension was stirred for 1 h at room temperature. The precipitate was collected to give a black solid, 12, in quantitative yield. The bisulfate salt 8a could be recovered by dissolving the complex 12 in excess concentrated sulfuric acid.

Reaction of Salt 7b with Tetrabutylammonium Iodide. To a solution of the salt 7b (0.05g, 0.068 mM) in 100 mL of dry acetonitrile was added dropwise a solution of 2 equivalents of tetrabutylammonium iodide in acetonitrile. The color of the solution changed from orange to green whereupon a black solid precipitated. The black, microcrystalline solid was collected and washed with acetonitrile to give the iodine complex 11 (0.037g, 80% yield), mp 301-302°C; UV (CH_3CN) λ_{max} 675 nm. Calcd. for $C_{28}H_8S_4I_{1.96}$: C, 45.98; H, 2.48; I, 34.01. Found: C, 46.19; H, 2.57; I, 34.25%. Reaction with lithium iodide was carried out in the same manner. The salt 6 was recovered by dissolving complex 11 into cold, concentrated acids.

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