SYNTHESIS OF NEW 8-PHENYL[1,2]DITHIOL[1,5-b]NAPHTHO[2,1-d]-
[1,2]DITHIOLE-10-S\textsuperscript{IV}, 2,5-DIPHENYL-3,4-DIHYDRO-1,6,6a-TRITHIA-
(6a-S\textsuperscript{IV})CYCLOPENTA[cd]PENTALENE AND 2,6-DIPHENYL-4,5-DIHYDRO-
3H-[1,2]DITHIOLO[4,5,1-hi][1,2]BENZODITHIOLE-8-S\textsuperscript{IV} DERIVATIVES

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Abstract — In order to investigate the anti-oxidant properties on
lubricant oils, 5,6-dihydro-8-phenyl[1,2]dithioolo[1,5-b]naphtho[2,1-
d][1,2]dithiole-10-S\textsuperscript{IV} and a number of phenyl substituted derivatives
have been synthesized by cyclization with P\textsubscript{2}S\textsubscript{5} of the corresponding
1,3,5-triketones in toluene. Moreover, some 2,5-diphenyl-3,4-dihydro-
1,6,6a-trithia(6a-S\textsuperscript{IV})cyclopenta[cd]pentalene and 2,6-diphenyl-4,5-
dihydro-3H-[1,2]dithioolo[4,5,1-hi][1,2]benzodithiole-8-S\textsuperscript{IV} derivati-
vies have been synthesized by cyclization with P\textsubscript{2}S\textsubscript{5} of the correspon-
ding 2,5-dibenzoylcyclopentanone and 2,6-dibenzoylcyclohexanone deri-
vatives in toluene.

In order to investigate their anti-oxidant properties on lubricant oils,
5,6-dihydro-8-phenyl[1,2]dithioolo[1,5-b]naphtho[2,1-d][1,2]dithiole-10-S\textsuperscript{IV} and
a number of phenyl substituted derivatives have been synthesized by cycliza-
tion with P\textsubscript{2}S\textsubscript{5} of the corresponding 1,3,5-triketones in toluene. Several com-
ounds containing sulfur or other hetero-atoms have been employed on account
of their anti-oxidant properties. They are characterized by well-defined chemi-
cal structures such as the alkylthiols, thioethers, disulfides, sulfoxides, sulfones, alkylphenol sulfides, aromatic amines, calcium, barium and aluminum dialkyl phosphates, zinc dialkyl and diaryl dithiophosphates. There are also a number of other compounds whose anti-oxidant activities cannot be easily predicted on the basis of their molecular structures. An example of such compounds is given by the thiathiophene (1) derivatives, where \( R_1, R_2, R_3 \) and \( R_4 \) may be alkyl, aryl or arylalkyl groups. Many of these derivatives have been tested successfully as anti-oxidant in the mineral oils. For such substances, the mechanism of action in relation to their molecular structures and the fact that they don't show always the same effect with respect of synthetic oils are still to be explained. Taking into account the utility of thiathiophene derivatives, we have synthesized some of the latter compounds to study their anti-oxidant activities.

Thiathiophenones may be obtained from \( \alpha \)-dithiopyrones with sodium sulfide in dimethyl sulfoxide (DMSO) and subsequent oxidation by potassium ferricyanide. Behringer and Grimm described the formation of derivatives of 1 by reaction of thioacetic acid with 2,4-pentanedione and various \( \alpha \)-acetylenic ketones. Other methods involved several steps. An alternative route for the synthesis of thiathiophenones is based on the reaction of \( P_2S_5 \) with carbonyl compounds. In this paper we report our investigation of the cyclization into thiothiophenones of a series of 1,3,5-triketones by \( P_2S_5 \). The triketones were prepared by benzoylation of 2-acetyl tetralone with alkyl benzoates in the presence of sodium hydride and using 1,2-dimethoxyethane as solvent. When 2-acetyl tetralone was allowed to react, under the same experimental conditions, with methyl 2,6-dichlorobenzoate, the following new compounds were obtained: 1-(2,6-dichlorophenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2m) and 1-(2-chloro-6-methoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naph-
thelynyl)-1,3-propanedione (2n). In order to explain the formation of 2n, it has been supposed that in the course of a Claisen-type reaction the leaving methoxyl group causes an aromatic nucleophilic substitution of a chlorine atom adjacent the ester function. In the presence of other solvents such as dioxane, the reaction has always led to the same products so excluding that the methoxyl group arises from the solvent (1,2-dimethoxyethane). Furthermore, in order to synthesize other 1,3,5-triketones, 2,5-bis[4-(1,1-dimethylethyl)benzoyl]cyclopentanone (4a), 2,5-bis[3,4-dimethoxybenzoyl]cyclopentanone (4b) and 2,6-bis-[4-(1,1-dimethylethyl)benzoyl]cyclohexanone (6), were prepared as usual by benzylation of cyclopentanone or cyclohexanone. The structures of all the triketones obtained have been supported by spectroscopic evidence. The nmr spectra showed signals characteristic of the keto-enolic structures. At this point, all the triketones obtained were easily transformed, in one step, into the corresponding thiathiophthenes.
4a, 5a: \( R_1 = H; \ R_2 = \text{C(CH}_3\text{)}_3 \)

4b, 5b: \( R_1, \ R_2 = \text{OCH}_3 \)
The cyclization of 1,3,5-triketones was carried out by treating a refluxing solution of triketones in toluene with $\text{P}_2\text{S}_5$. The compounds were isolated by treatment with ethanol (in which they are little soluble) of the solid material obtained after evaporation of toluene solution previously washed with KOH aqueous and successively with water until neutral. All the compounds gave satisfactory elemental analyses; ir, nmr and mass spectra were in agreement with the structures reported.

EXPERIMENTAL

Melting points were determined on Büchi 510 apparatus and are uncorrected. Ir spectra have been recorded in nujol with a Perkin-Elmer 137 ir spectrophotometer. Nmr spectra have been obtained with a Varian EM-360 at 60 MHz with tetramethyleilane as internal standard. Mass spectra were recorded on a Jeol JMS-105G-2 mass spectrometer. Elemental analyses were carried out by the Kurt Eder service (Geneve, Suisse).

Synthesis of the 1,3,5-Triketones. General Procedure

A suspension of sodium hydride (dispersion 55-60% in oil) 10.5 g (0.25 mole) in 100 ml of 1,2-dimethoxyethane was added dropwise to a stirred solution of carbonylic compound (2-acetyltetralone, cyclopentanone or cyclohexanone) (0.05 mole) and benzoic ester derivative (0.075 mole for 2-acetyltetralone and 0.15 mole for cyclopentanone or cyclohexanone) in 100 ml of 1,2-dimethoxyethane. The mixture with 2-acetyltetralone was refluxed for 6 h, the mixture with cyclopentanone or cyclohexanone for 2 h. Most of the solvent was then removed under reduced pressure and the pasty residue was cooled to 0°C in an ice-water bath. Diethyl ether (150 ml) was added. After stirring the mixture for a few min, 100 ml of cold water was added dropwise until the excess sodium hydride was destroyed. The two layers were separated. The ethereal layer was extracted twice with 100 ml of cold 1% aqueous sodium hydroxide. Then 200 g of crushed ice and successively 50 ml of 12 N hydrochloric acid were added at the aqueous extracts combined. The mixture was stirred for 20 min. After filtration, the resinous product obtained was dissolved in chloroform and then washed with water until
neutral. After drying (anhydrous sodium sulfate), the solvent was evaporated in vacuo and the residue treated with ethanol to yield a crude product.

1-(2,6-Dichlorophenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2m) and 1-(2-chloro-6-methoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2n).

The crude product obtained from the reaction of 2-acetyltetralone with methyl 2,6-dichlorobenzoate was chromatographed over a column of silica gel (cyclohexane/ethyl acetate 95:5) to give 2m and 2n.

Compound 2m had mp 139-140 °C (from ethanol, yield 20%); ir (nujol): 1580-1605 cm⁻¹; ¹H-nmr (CDCl₃): δ 2.10-3.10 (m,4H,C₃-H and C₄-H); 6.90-8.00 (m,7H,aromatic H); 4.05, 5.75, 15.00 and 16.15 (4s,3H,C²-H and CO-CH₂-CO, keto-enolic structure); ms/m/z 360 (M⁺). Anal. Calcd for C₁₉H₁₄Cl₂O₃: C, 63.15; H, 3.87; Cl, 19.66. Found: C, 63.02; H, 4.24; Cl, 19.31.

Compound 2n had mp 102-103 °C (from ethanol, yield 43%); ir (nujol): 1580-1605 cm⁻¹; ¹H-nmr (CDCl₃): δ 2.30-3.10 (m,4H,C₃-H and C₄-H); 3.80 (s,3H,CH₃); 6.70-8.00 (m,7H,aromatic H); 4.05, 5.80, 15.10 and 16.30 (4s,3H,C²-H and CO-CH₂-CO, keto-enolic structure); ms/m/z 356 (M⁺). Anal. Calcd for C₂₀H₁₇ClO₄: C, 67.32; H, 4.80; Cl, 9.94. Found: C, 67.31; H, 4.98; Cl, 10.31.

2,5-Bis[4-(1,1-dimethylethyl)benzoyl]cyclopentanone (4a).

This compound was obtained in 69% yield from reaction of cyclopentanone with methyl 4-tert-butylbenzoate, mp 160-161 °C (ethanol); ir (nujol): 1590 cm⁻¹; ¹H-nmr (CDCl₃): δ 1.30 [s,18H,C(CH₃)₃]; 2.20-3.20 (m,4H,C₃-H and C₄-H); 7.10-8.20 (m,8H,aromatic H); 4.50, 13.60 and 14.10 (2H,C²-H and C⁵-H keto-enolic structure); ms/m/z 404 (M⁺). Anal. Calcd for C₂₇H₃₂O₃: C, 80.16; H, 7.97. Found: C, 80.23; H, 8.02.

2,5-Bis(3,4-dimethoxybenzoyl)cyclopentanone (4b).

This compound was obtained in 72% yield from reaction of cyclopentanone with methyl 3,4-dimethoxybenzoate, mp 155-156 °C (ethanol); ir (nujol): 1595-1625 cm⁻¹; ¹H-nmr (CDCl₃): δ 2.20-3.20 (m,4H,C₃-H and C₄-H); 3.90 (s,12H,CH₃); 6.70-7.80 (m,6H,aromatic H); 4.50 and 14.70 (2H,C²-H and C⁵-H keto-enolic structure); ms/m/z 412 (M⁺). Anal. Calcd for C₂₃H₂₄O₇: C, 66.98; H, 5.87. Found: C, 66.99; H, 5.93.
This compound was obtained in 80% yield from reaction of cyclopentanone with methyl 4-tert-butylbenzoate, mp 163-164 °C (ethanol); ir (nujol): 1575-1605 cm⁻¹; ¹H-nmr (CDCl₃): δ 1.30 [s, 18H, CH₃]; 1.80-2.70 (m, 6H, C⁴-H and C⁵-H); 7.05-8.00 (m, 8H, aromatic H); 4.45, 15.55 and 16.55 (2H, C⁴⁻H and C⁵⁻H, keto-enolic structure); ms: m/z 418 (M⁺). Anal. Calcd for C₂₈H₃₄O₃: C, 80.34; H, 8.19. Found: C, 80.36; H, 8.18.

Synthesis of Thiathiophthenes. General Procedure.
P₂S₅ (6g, 0.03 mole) was added slowly to a solution of 1,3,5 triketone (0.01 mole) in toluene (300mL). The resulting suspension was refluxed for 2 h. After cooling the reaction mixture was filtered. The filtrate was treated with 100 mL of 3% aqueous potassium hydroxide and with water (3x100mL) until neutral and evaporated under reduced pressure. The residue was treated with warm ethanol (10mL) and filtered off to yield a crude product.

5,6-Dihydro-8-phenyl[1,2]dithiolo[1,5-b]naphtho[2,1-d][1,2]-dithiole-10-S⁻ IV (3a).
This compound was obtained in 44% yield from reaction of 1-phenyl-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2a) with P₂S₅; mp 151-152 °C (chloroform-ethanol); ¹H-nmr (CDCl₃): δ 3.00-3.40 (m, 4H, CH₂-CH₂); 7.30-8.10 (m, 9H, aromatic H); 8.25 (s, 1H, C⁷⁻H); ms: m/z 338 (M⁺). Anal. Calcd for C₁₉H₁₄S₃: C, 67.41; H, 4.17; S, 28.41. Found: C, 67.21; H, 4.36; S, 28.17.

5,6-Dihydro-8-(2-methoxyphenyl)[1,2]dithiolo[1,5-b]naphtho[2,1-d][1,2]-dithiole-10-S⁻ IV (3b).
This compound was obtained in 58% yield from reaction of 1-(2-methoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2b) with P₂S₅; mp 192-193 °C (chloroform-ethanol); ¹H-nmr (CDCl₃): δ 2.90-3.20 (m, 4H, CH₂-CH₂); 3.80 (s, 3H, OCH₃); 6.80-7.35 and 7.40-8.00 (2m, 8H, aromatic H); 8.30 (s, 1H, C⁷⁻H); ms: m/z 368 (M⁺). Anal. Calcd for C₂₀H₁₆O₃S: C, 65.18; H, 4.38; S, 26.10. Found: C, 65.00; H, 4.51; S, 26.09.

5,6-Dihydro-8-(2-ethoxyphenyl)[1,2]dithiolo[1,5-b]naphtho[2,1-d][1,2]-dithiole-10-S⁻ IV (3c).
This compound was obtained in 59% yield from reaction of 1-(2-ethoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2c) with P₂S₅; mp 183-185 °C (acetic anhydride); ¹H-nmr (CDCl₃): δ 2.90-3.20 (m, 4H, CH₂-CH₂); 4.00 (t, 4H, CH₂); 7.30-8.10 (m, 9H, aromatic H); 8.30 (s, 1H, C⁷⁻H); ms: m/z 368 (M⁺). Anal. Calcd for C₂₀H₁₆O₃S: C, 65.18; H, 4.38; S, 26.10. Found: C, 65.00; H, 4.51; S, 26.09.
n~ll-3-(1,2,3,4-tetrah~dro-l-oxo-2-naphthalenyll-1,3-propanedione (2c) with P2S5; mp 157-158 °C (chloroform-ethanol); 1H-nmr (CDCl3): δ 1.45 (t, J=6 Hz, 3H, OCH2-CH3); 2.90-3.20 (m, 4H, CH2-CH2); 4.10 (q, J=6Hz, 2H, OCH2-CH3); 6.75-7.40 and 7.60-7.90 (2m, 8H, aromatic H); 8.45 (s, 1H, C7H); ms: m/z 382 (M+). Anal. Calcd for C21H18O3S3: C, 65.91; H, 4.74; S, 25.16. Found: C, 66.11; H, 4.93; S, 25.30.

5,6-Dihydro-8-(2-proproxyphenyl)[1,2]dithiolo[1,2-b]naphtho[2,1-d][1,2]dithio-10-s IV (3d):
This compound was obtained in 43 % yield from reaction of 1-(2-propoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2d) with P2S5; mp 153-154 °C (chloroform-ethanol); 1H-nmr (CDCl3): δ 1.05 (t, J=6 Hz, 3H, OCH2-CH2-CH3); 1.75 (sext, J=6Hz, 2H, OCH2-CH2-CH3); 2.90-3.25 (m, 4H, CH2-CH2); 4.00 (t, J=6Hz, 2H, OCH2-CH2-CH3); 6.75-7.49 and 7.45-8.00 (2m, 8H, aromatic H); 8.45 (s, 1H, C7H); ms: m/z 396 (M+). Anal. Calcd for C22H20O3S3: C, 66.63; H, 5.08; S, 24.25. Found: C, 66.83; H, 5.23; S, 24.28.

8-(2-Chlorophenyl)-5,6-dihydro-[1,2]dithiolo[1,2-b]naphtho[2,1-d][1,2]dithio-10-s IV (3e):
This compound was obtained in 32 % yield from reaction of 1-(2-chlorophenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2e) with P2S5; mp 188-189 °C (chloroform-ethanol); 1H-nmr (CDCl3): δ 3.05-3.35 (m, 4H, CH2-CH2); 7.20-7.70 (m, 8H, aromatic H); 8.15 (s, 1H, C7H); ms: m/z 372 (M+). Anal. Calcd for C19H13Cl3S3: C, 61.18; H, 3.51; Cl, 9.52; S, 25.73. Found: C, 60.99; H, 3.68; Cl, 9.78; S, 25.51.

5,6-Dihydro-8-(4-methoxyphenyl)[1,2]dithiolo[1,2-b]naphtho[2,1-d][1,2]dithio-10-s IV (3f):
This compound was obtained in 37% yield from reaction of 1-(4-methoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2f) with P2S5; mp 139-140 °C (chloroform-ethanol); 1H-nmr (CDCl3): δ 3.00-3.30 (m, 4H, CH2-CH2); 3.90 (s, 3H, OCH3); 7.00 and 7.90 (2d, J=9Hz, 4H, aromatic H); 7.25-7.60 and 7.75-8.05 (2m, 4H, aromatic H); 8.20 (s, 1H, C7H); ms: m/z 368 (M+). Anal. Calcd. for C20H16O3S3: C, 65.18; H, 4.38; S, 26.10. Found: C, 65.42; H, 4.58; S, 26.04.
This compound was obtained in 44% yield from reaction of 1-[4-(1,1-di-methylethyl)phenyl]-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthaleny1)-1,3-propanedione (2g) with P2S5; mp 163-164 °C (chloroform-ethanol); 1H-nmr (CDCl3): δ 1.30 (s, 3H, C(CH3)2; 3.00-3.30 (m, 4H, CH2-CH2); 7.10-7.55 and 7.65-7.90 (2m, 4H, aromatic H); 7.35 and 7.75 (2d, J=9Hz, 4H, aromatic H); 8.10 (s, 1H, C7-H); ms: m/z 394 (M+).

Anal. Calcd for C23H22S3: C, 70.00; H, 5.62; S, 24.37. Found: C, 70.18; H, 5.80; S, 24.29.

This compound was obtained in 45% yield from reaction of 1-(4-chlorophenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (a) with P2S5; mp 175-176 °C (chloroform-ethanol); 1H-nmr (CDCl3): δ 3.00-3.40 (m, 4H, CH-CH2); 7.30-7.70 and 7.80-8.10 (2m, 4H, aromatic H); 7.55 and 7.95 (2d, J=9Hz, 4H, aromatic H); 8.30 (s, 1H, C7-H); ms: m/z 372 (M+). Anal. Calcd for C19H13ClS3: C, 61.19; H, 3.51; Cl, 9.51; S, 25.79. Found: C, 60.93; H, 3.79; Cl, 9.42; S, 25.48.

This compound was obtained in 32 % yield from reaction of 1-(2,5-dichlorophenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2i) with P2S5; mp 131-132 °C (chloroform-ethanol); 1H-nmr (CDCl3): δ 2.95-3.20 (m, 4H, CH2-CH2); 7.15-7.40 and 7.45-7.55 (2m, 7H, aromatic H); 8.00 (s, 1H, C7-H); ms: m/z 406 (M+). Anal. Calcd for C19H12Cl2S3: C, 56.01; H, 2.97; Cl, 17.41; S, 23.61. Found: C, 56.05; H, 2.99; Cl, 17.17; S, 23.69.

This compound was obtained in 39 % yield from reaction of 1-(5-chloro-2-methoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2j) with P2S5; mp 205-206 °C (chloroform-ethanol); 1H-nmr (CDCl3): δ 3.05-3.30 (m, 4H, CH2-CH2); 3.95 (s, 3H, OCH3) 6.90-7.80 (m, 7H, aromatic H); 8.40 (s, 1H, C7-H);
ms:m/z 402 (M^+). Anal. Calcd for C_{20}H_{15}ClO_{3}: C, 59.61; H, 3.75; Cl, 8.80; S, 23.87. Found: C, 59.71; H, 4.00; Cl, 9.03; S, 23.86.

8-(5-Chloro-2-ethoxyphenyl)-5,6-dihydro-[1,2]dithiole-[1,5-b]naphtho[2,1-d]-[1,2]dithiole-10-SIV (3a).
This compound was obtained in 41 % yield from reaction of 1-(5-chloro-2-ethoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2k) with P_{2}S_{5}; mp 177-178 °C (chloroform-ethanol); ^1H-nmr (CDCl_{3}): δ 1.45 (t, J=7 Hz,3H,OC{H}_{2}-CH_{3}); 2.95-3.25 (m,4H,CH_{2}-CH_{2}); 4.10 (q, J=7Hz,2H,OC{H}_{2}-CH_{3}); 6.70-7.90 (m,7H,aromatic H); 8.40 (s,1H,C{^7}-H); ms:m/z 416 (M^+). Anal. Calcd for C_{21}H_{17}ClO_{3}: C, 60.48; H, 4.11; Cl, 8.50; S, 23.07. Found: C, 60.52; H, 4.13; Cl, 8.44; S, 22.88.

8-(5-Chloro-2-propoxyphenyl)-5,6-dihydro-[1,2]dithiole-[1,5-b]naphtho[2,1-d]-[1,2]dithiole-10-SIV (3b).
This compound was obtained in 42 % yield from reaction of 1-(5-chloro-2-propoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2l) with P_{2}S_{5}; mp 134-135 °C (chloroform-ethanol); ^1H-nmr (CDCl_{3}): δ 1.05 (t, J=7 Hz,3H,OC{H}_{2}-CH_{2}-CH_{3}); 1.80 (sext, J=7Hz,2H,OC{H}_{2}-CH_{2}-CH_{3}); 2.80-3.30 (m,4H,CH_{2}-CH_{2}); 3.95 (t, J=7Hz,2H,OC{H}_{2}-CH_{2}-CH_{3}); 6.60-7.90 (m,7H,aromatic H); 8.40 (s,1H,C{^7}-H); ms:m/z 430 (M^+). Anal. Calcd for C_{22}H_{19}ClO_{3}: C, 61.28; H, 4.44; Cl, 8.23; S, 22.34. Found: C, 61.43; H, 4.53; Cl, 8.29; S, 22.38.

8-(2,6-Dichlorophenyl)-5,6-dihydro-[1,2]dithiole-[1,5-b]naphtho[2,1-d]-[1,2]dithiole-10-SIV (3m).
This compound was obtained in 22 % yield from reaction of 1-(2,6-dichlorophenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2m) with P_{2}S_{5}; mp 187-188 °C (chloroform-ethanol); ^1H-nmr (CDCl_{3}) δ 2.80-3.20 (m,4H,CH_{2}-CH_{2}); 6.75 (s,1H,C{^7}-H); 7.10-7.45 and 7.60-7.90 (m,7H,aromatic H); ms:m/z 406 (M^+). Anal. Calcd for C_{19}H_{12}Cl_{2}S_{3}: C, 56.03; H, 2.97; Cl, 17.43; S, 23.57. Found: C, 55.96; H, 2.80; Cl, 17.21; S, 23.51.

8-(2-Chloro-6-methoxym phenyl)-5,6-dihydro-[1,2]dithiole-[1,5-b]naphtho[2,1-d]-[1,2]dithiole-10-SIV (3n).
This compound was obtained in 38 % yield from reaction of 1-(2-chloro-6-methoxym phenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2n)
with $\text{P}_2\text{S}_5$; mp 202-203 °C (chloroform-ethanol); $^1\text{H}$-nmr (CDCl$_3$): $\delta$ 3.00-3.30 (m, 4H, CH$_2$-CH$_2$); 3.85 (s, 3H, OCH$_3$); 6.80-7.90 (m, 7H, aromatic H); 8.20 (s, 1H, C$_7^-$-H);
ms: m/z 402 (M$^+$). Anal. Calcd for C$_{20}$H$_{15}$ClO$_3$: C, 59.61; H, 3.76; Cl, 8.82; S, 23.85. Found: C, 58.94; H, 3.75; Cl, 10.01; S, 23.51.

2,5-Bis[4-(1,1-dimethylethyl)phenyl]-3,4-dihydro-1,6,6a-trithia(6a-$^\text{IV}$)cyclopenta[cd]pentalene (5a).

This compound was obtained in 60% yield from reaction of 2,5-bis[4-(1,1-dimethylethyl)benzoyl]cyclopentanone (4a) with $\text{P}_2\text{S}_5$; mp 280-281 °C (chloroform-ethanol); $^1\text{H}$-nmr (CDCl$_3$): $\delta$ 1.30 (s, 18H, C(CH$_3$)$_3$); 3.45 (s, 4H, C$_3^-$-H and C$_4^-$-H); 7.10-7.70 (m, 8H, aromatic H); ms: m/z 450 (M$^+$). Anal. Calcd for C$_{27}$H$_{30}$S$_3$: C, 71.95; H, 6.71; S, 21.34. Found: C, 71.93; H, 6.74; S, 21.26.

2,5-Bis[3,4-dimethoxyphenyl]-3,4-dihydro-1,6,6a-trithia(6a-$^\text{IV}$)cyclopenta[cd]pentalene (5b).

This compound was obtained in 40% yield from reaction of 2,5-bis[3,4-dimethoxybenzoyl]cyclopentanone (4b) with $\text{P}_2\text{S}_5$; mp 173-174 °C (chloroform-ethanol); $^1\text{H}$-nmr (CDCl$_3$): $\delta$ 3.90 (s, 12H, OCH$_3$); 3.50 (s, 4H, C$_3^-$-H and C$_4^-$-H); 7.00-7.40 (m, 6H, aromatic H); ms: m/z 458 (M$^+$). Anal. Calcd for C$_{23}$H$_{22}$O$_4$S$_3$: C, 60.26; H, 4.80; S, 20.96. Found: C, 60.01; H, 4.84; S, 21.06.

2,6-Bis[4-(1,1-dimethylethyl)phenyl]-4,5-dihydro-3H-[1,2]dithiolo[4,5,1-bi]-[1,2]benzodithiole-8-$^\text{S}^-$-$^\text{IV}$ (7).

This compound was obtained in 58% yield from reaction of 2,6-bis[4-(1,1-dimethylethyl)benzoyl]cyclohexanone (6) with $\text{P}_2\text{S}_5$; mp 277-278 °C (chloroform-ethanol); $^1\text{H}$-nmr (CDCl$_3$): $\delta$ 1.25 (s, 18H, C(CH$_3$)$_3$); 1.60-1.90 (m, 2H, C$_4^-$-H); 2.60-3.10 (m, 4H, C$_3^-$-H and C$_5^-$-H); 7.20 (s, 8H, aromatic H); ms: m/z 464 (M$^+$). Anal. Calcd for C$_{28}$H$_{32}$S$_3$: C, 72.36; H, 6.94; S, 20.70. Found: C, 72.33; H, 6.94; S, 20.80.

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REFERENCES

2) E. Rossi and S. Fattori (Snamprogetti), "Lubricating Compositions Inhibited from Oxidation", USA patent 3,816,312, July 11, 1974.

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