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TETRAHEDRON

Efficient Condensation of *p*-Substituted Phenols, *p*-Thiocresol and 2,7-Dihydroxynaphthalene with Malonaldehyde Tetramethyl Acetal in Trifluoroacetic Acid

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Abstract: Condensation reactions of malonaldehyde tetramethyl acetal with *p*-substituted phenol derivatives and *p*-thiocresol have been carried out in trifluoroacetic acid and the corresponding methano-dibenzo[1,3]-dioxocins and dithiocin type compounds were obtained in good to excellent yields. In the case of condensation of 2,7-dihydroxynaphthalene with malonaldehyde tetramethyl acetal 8,16-methano-16H-dinaphtho[2,1-d:1',2'-g]-[1,3]dioxocin-2,14-diol was obtained in high yield.

INTRODUCTION

Condensation of unsubstituted phenols with glyoxal bisulfate or with glyoxal has been reported to produce insoluble resins,[1,2] while *p*-substituted phenols were reported to yield compounds having the acetal type structures (**1**) and (**2**), namely 5a,10b-dihydrobenzofuro[2,3-b] benzofurans[3,4] and 7a,14c-dihydronaphtho [2,1-b]naphtho[2′,1′: 5,6]furo[3,2-d]furan.[5,6] These types of acetalic structures with dihydro-, tetrahydro- and hexahydrofuro[2,3-b]furan moieties are often found in natural products (e.g., the extracts from leaves of various plants[7a-c] such as clerodendrin A as a diterpene, aflatoxin[8] and asteltoxin[9]). The preparation of novel aromatic compounds with one or two dihydrofurofuran moieties starting from 2-naphthol and glyoxal has been reported.[10]

Condensation reactions of 4,4′-isopropylidene diphenol (bisphenol–A) and dihydroxy naphthalenes with glyoxal in the presence of sulfuric acid and methanesulfonic acid and formation of ladder type polymers were reported recently.[11] Similar condensation polymers from diphenols and glyoxal together with their structure elucidation have also been reported by Akar[12] *et al.*

Recently, the base catalyzed reaction of 2-naphthol with glyoxal was also investigated in which the final product was considered to be similar to that obtained from the acid catalyzed reaction[13]. Condensation of malonaldehyde or malonaldehyde bisulfate with 2-naphthol in the presence of formic acid at 50-60°C has been shown to give 8,16-methano-16H-dinaphtho[2,1-d:1′,2′-g][1,3]dioxocin (**3**)[14] in only 23% yield.

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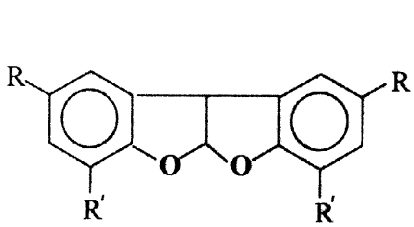
However, condensations of malonaldehyde with other phenol derivatives have not been reported as far as we know. In the course of our studies on the synthesis of thermally stable polymers[15-17] from **1a** derivatives



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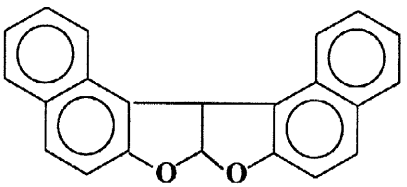

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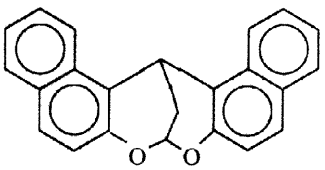


3

(a) R=CH_3 , R′=H

(b) R=CH_3 , R′=$C(CH_3)_3$

(c) R=Cl, R′=H

Scheme 1

and our ongoing research on the development of new thermally stable polymers from condensation of diphenols and dialdehydes, we have also studied synthetic routes towards new methano-dibenzo[1,3]dioxocins and dithiocin type compounds and their related derivatives as new model compounds which in some cases can be used as important monomers for the preparation of a variety of thermally stable polymers.

RESULTS AND DISCUSSION

In order to investigate the possibility of using the reported method[14] for condensation of 2-naphthol and malonaldehyde or malonaldehyde bisulfate with different phenols, we performed the reaction of phenols with malonaldehyde or malonaldehyde bisulfate under the reported[14] conditions. We observed that this method cannot work for phenolic compounds and self condensation of malonaldehyde occurs more rapidly than its condensation with phenols. A similar observation for the reaction of acetaldehyde and 2-naphthol has also been reported in the literature.[18] We therefore decided to develop a new synthetic method for the synthesis of the above class of compounds.

We studied the possibility of condensation of different phenols with malonaldehyde tetramethyl acetal in acetic acid in the presence of methanesulfonic acid as catalyst. Condensation of phenols with malonaldehyde tetramethyl acetal occurred and the corresponding methano-dibenzo[1,3]dioxocins compounds were obtained in low to moderate yields. In order to increase the yields of the products, we tried the same reactions using trifluoroacetic acid as both solvent and catalyst. The reaction of phenols carrying alkyl groups (**4a-c**) or having both alkyl and halogen (**4d**) gave excellent yields of their corresponding 6,12-methano-12H-dibenzo[2,1-d:1′,2′-g][1,3]dioxocins **7a-e**. The reaction of phenols carrying only halogens (**4e,4f**) gave moderate yields (Scheme3). The results with the structurally different *p*-substituted phenolic compounds are shown in the Table. Condensation of 2-naphthol with malonaldehyde or malonaldehyde-

bisulfate has been reported to produce only 23% of 8,16-methano-16 H-dinaphtho [2,1-d:1′,2′-g] [1,3]dioxocin.

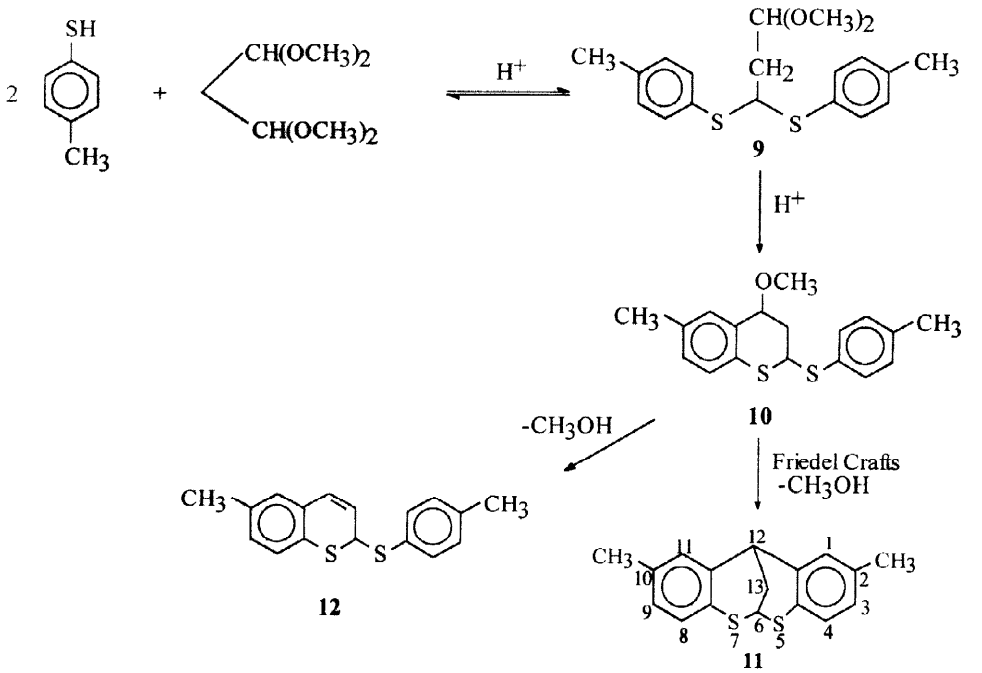
Table : Reaction of phenolic compounds (**4a-f**) with malonaldehyde tetramethyl acetal.

Phenolic compounds	Reaction conditions[(a)]	Time(h)	Yield(%)
7a	CF_3CO_2H	4	91
	CH_3SO_3H/HOAc	9	68
7b	CF_3CO_2H	4	92
	CH_3SO_3H/HOAc	8	66
7c	CF_3CO_2H	4	91
	CH_3SO_3H/HOAc	8	65
7d	CF_3CO_2H	4	90
	CH_3SO_3H/HOAc	9	64
7e	CF_3CO_2H	36	52
	CH_3SO_3H/HOAc	36	24
7f	CF_3CO_2H	48	36
	CH_3SO_3H/HOAc	48	11
7g	CF_3CO_2H	48	–[b]
	CH_3SO_3H/HOAc	48	–

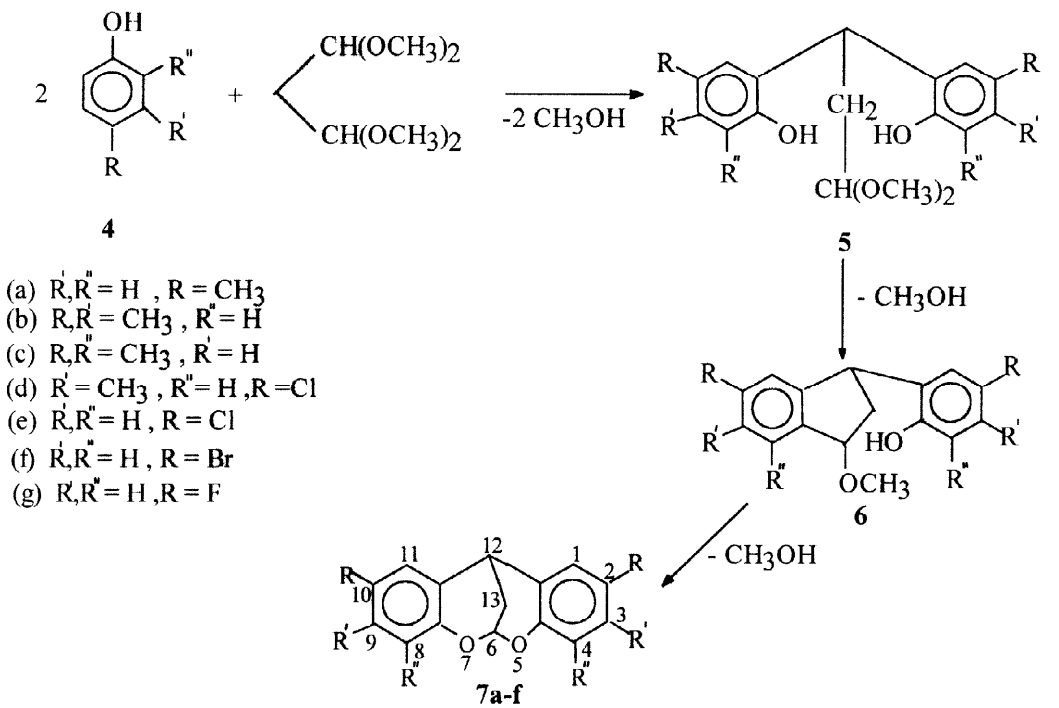
(a) All of the reactions were carried out at r.t.
(b) No reaction

We therefore applied our method for the condensation of 2-naphthol and malonaldehyde tetramethyl-acetal and the yield was increased to 88%. We next decided to see the possibility of applying our method to condensation of thiophenols. We studied the condensation of *p*-thiocresol with malonaldehyde tetramethyl-acetal under both reaction conditions. From this reaction , compound **11** was obtained in 25% yield together with the product **12** in 14% yield. The formation of compound **12** from the reaction of *p*-thiocresol with malonaldehyde tetramethyl acetal under these conditions may occur through the intermediate **9** followed by a successive Friedel-Crafts reaction and formation of **10** which can produce compound **12** through elimination of methanol or **11** through intramolecular Friedel-Crafts reaction (Scheme 2). This is similar to the reported results on the condensation of 2-thionaphthol.[19,20] On the other hand, condensation of two moles of phenols with malonaldehyde tetramethyl acetal occurs first through a Friedel-Crafts reaction to give **5** followed by an intramolecular acetalization reaction[18] (Scheme 3).

We next applied our method for the synthesis of 8,16-methano-16H-dinaphtho-[2,1-d:1′,2′-g][1,3]-dioxocin – 2,14-diol **8** as a new monomer from 2,7-dihydroxy naphthalene.

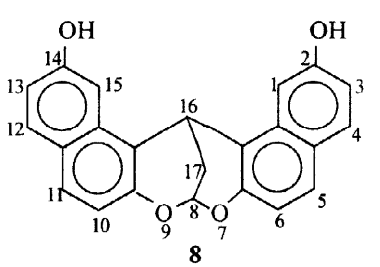


Scheme 2



(a) R',R" = H , R = CH_3
(b) R,R' = CH_3 , R" = H
(c) R,R" = CH_3 , R' = H
(d) R' = CH_3 , R" = H ,R = Cl
(e) R',R" = H , R = Cl
(f) R',R" = H , R = Br
(g) R',R" = H ,R = F

Scheme 3



Condensation reactions of dihydroxy naphthalenes and malonaldehyde tetramethyl acetal have resulted in either dimeric or polymeric products depending on the position of the hydroxyl groups. When we treated 2,7-dihydroxynaphthalene with malonaldehyde tetramethyl acetal in acetic acid-methanesulfonic acid or in trifluoroacetic acid 8,16-methano-16H-dinaphtho[2,1-d:1′,2′-g][1,3]dioxocin-2,14-diol **8** was obtained in 48% and 81% yields respectively.Condensation of 2,6-, 1,5- and 2,3-dihydroxy naphthalene produced polymers whose structures are under investigation.[21] The reason that 2,7-dihydroxy naphthalene gives the dimer **8** but 2,6-, 1,5-, 2,3- dihydroxy naphthalenes give polymers is probably due to the steric effect on **8** which prevents its further condensation with malonaldehyde tetramethyl acetal.

In conclusion, the efficiency and simplicity of this method, the moderate to excellent yield of the products and the possibility of applying this method to phenols, thiophenols and naphthols make this method very useful for this type of transformation in organic synthesis.

EXPERIMENTAL

General methods: Solvents and chemical materials were obtained from Merck chemical company (Germany) and Fluka (Switzerland). Melting points were determined with a Buchi 535 melting point apparatus. IR spectra were recorded on a perkin Elmer 781 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 250 MHz Bruker Advanced DPX-250 spectrometer using tetramethylsilane (TMS) as an internal standard. Mass spectra (MS) were performed with a GCMS-QP 1000 EX at 70 eV (Shimadzo). UV spectra were recorded on a Pharmacia Biotech Ultraspec 3000 model 80-2106-20 spectrometer.

General procedures for (7a-f):

Method A: Phenolic compounds (**4a-f**) (50 mmol), malonaldehyde tetramethyl acetal 4mL (25 mmol) and trifluoroacetic acid (10-15) mL was allowed to stand for 4-48 h at room temperature. The reaction mixture solidified. After addition of acetic acid (20-30) mL, the crude product was collected by filtration and washed with methanol, boiled with water. Reaction products were purified by appropriate methods specified below.

Method B: Phenolic compounds (**4a-f**) (50 mmol) in acetic acid (10-15)mL and malonaldehyde tetramethyl acetal 4mL (25 mmol) were mixed in a round- bottomed flask at room temperature. Methane sulfonic acid (4-5) mL was then added very slowly under stirring.The reaction was then stirred at room temperature for 8-48 h. After this time, the reaction mixture solidified gradually.The crude product was collected by filtration and washed with acetic acid and methanol, and boiled with water. Reaction products were purified by appropriate methods specified below.

2,10-Dimethyl-6,12-methano-12H-dibenzo[2,1-d:1′,2′-g][1,3]dioxocin (7a):

7a was obtained from **4a** and malonaldehyde tetramethyl acetal following the general procedure and purified by recrystallizing from ethanol-acetone (3/1,v/v) mixture to give white solid; mp=176-177°C; [Found: C, 80.8; H, 6.32. $C_{17}H_{16}O_2$ requires C, 80.95; H, 6.34%]; UV (CH_2Cl_2)λ 291 (ε_{max}=29730), 238 nm (ε=24400); ν_{max}(KBr) 2990-2900, 1240, 1180, 1075cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2.1-2.2 (8H, m, -C<u>H</u>$_3$, -C<u>H</u>$_2$), 3.65 (1H, t,

J 1.3 Hz, 12-H), 5.8 (1H, t, *J* 2 Hz, 6-H), 6.5-6.8 (6H, m, Ph); δ_C (62.9 MHz, $CDCl_3$) 22.8 (CH_3), 28 (12-C), 34.2 (13-C), 93.6 (6-C), 118.5, 128.4, 129.5, 130.6 and 131.7 (aromatic C), 151 (=CO); *m/z* (EI) 252 (72, MH^+), 237 (55), 235 (9.8), 146 (5.9), 145(100), 115 (14), 91 (5.9), 57 (8.8), 44 (9.8%).

2,3,9,10-tetramethyl-6,12-methano-12H-dibenzo[2,1-d:1′,2′-g][1,3]dioxocin (7b):

7b was obtained from **4b** and malonaldehyde tetramethyl acetal following the general procedure and purified by recrystallizing from acetic acid to give white solid; mp=230-231°C; [Found: C, 81.13; H, 7.24. $C_{19}H_{20}O_2$ requires C, 81.4; H, 7.15%]; UV(CH_2Cl_2) λ 292 (ε_{max} =22270), 234 nm (ε=19610); ν_{max}(KBr) 3000-2900, 1235, 1165, 1080 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2-2.218 (14H, m,-CH_3, -CH_2), 3.65 (1H, t, *J* 1.2 Hz, 12-H), 5.92 (1H, t, *J* 1.75 Hz, 6-H), 6.54 (2H, s, Ph), 6.75 (2H, s, Ph); δ_C (62.9 MHz, $CDCl_3$) 19.2 and 19.9 (CH_3), 26.5 (12-C), 31.4 (13-C), 92.5 (6-C), 117.8, 124.6, 128.5, 129.6 and 136.6 (aromatic C), 149.2 (=CO); *m/z* (EI) 280 (79, MH^+), 266 (20.4), 265 (82), 237 (12), 160 (13.2), 159 (100), 115 (17.8), 97 (23), 69 (50), 55 (56), 43 (100%).

2,4,8,10-tetramethyl-6,12-methano-12H-dibenzo[2,1-d:1′,2′-g][1,3]dioxocin (7c):

7c was obtained from **4c** and malonaldehyde teteramethyl acetal following the general procedure and purified by recrystallizing from acetic acid to give white solid; mp=186-187°C; [Found: C, 81.23; H, 7.24. $C_{19}H_{20}O_2$ requires C, 81.4; H, 7.15%]; UV(CH_2Cl_2)λ 290 (ε_{max}=27030), 239 nm (ε=26080); ν_{max}(KBr) 2990-2900, 1230, 1175, 1070 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2-2.38 (14H, m, -CH_3, -CH_2), 3.68 (1H, t, *J* 1.5 Hz, 12-H), 6 (1H, t, *J* 1.75 Hz, 6-H), 6.4-6.7 (4H, m, Ph); δ_C (62.9 MHz, $CDCl_3$) 18.27 and 22.8 (CH_3), 28 (12-C), 34.4 (13-C), 93.8 (6-C), 125.8, 127.3, 128.1, 131.24 and 132.15 (aromatic C), 148.5 (=CO); *m/z* (EI) 280 (75, MH^+), 265 (82), 237 (15), 160 (12.3), 159 (100), 115 (14), 91 (12), 77 (8.2), 65 (15.5), 55 (2.8), 43 (5.5%).

2,10-Dichloro-3,9-Dimethyl-6,12-methano-12H-dibenzo[2,1-d:1′,2′-g][1,3]dioxocin (7d):

7d was obtained from **4d** and malonaldehyde tetramethyl acetal following the general procedure and purified by recrystallizing from acetic acid to give white solid; mp=253-254°C; [Found:C, 63.54; H, 4.51. $C_{17}H_{14}O_2Cl_2$ requires C, 63.55; H, 4.36%]; UV(CH_2Cl_2)λ 294 (ε_{max}=26100), 237 nm (ε=24560); ν_{max}(KBr) 2990-2900, 1245, 1150, 1080 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2.15 (2H, dd, *J* 2.4 ,0.85 Hz, -CH_2), 2.24 (6H, s, -CH_3), 3.76 (1H, t, *J* 1.27 Hz, 12-H), 5.98 (1H, t, *J* 1.75 Hz, 6-H), 6.7 (2H, s, Ph), 7.2 (2H, s, Ph); δ_C (62.9 MHz, $CDCl_3$) 19.84 (CH_3), 25.32 (12-C), 30.6 (13-C), 92 (6-C), 118.8, 125.2, 126.3, 127.2, and 135.92 (aromatic C), 149.2 (=CO); *m/z* (EI) 321 (18, MH^+), 322 (30, MH^++1), 323 (6.7, MH^++2), 324 (4.7, MH^++3), 320 (48), 288 (2), 287 (12.4), 286 (7.2), 285(40), 182 (3), 181 (31.8), 180 (12.4), 179 (100), 115 (25), 77 (15), 51 (25%).

2,10-Dichloro-6,12- methano-12H-dibenzo[2,1-d:1′,2′-g][1,3]dioxocin (7e):

7e was obtained from **4e** and malonaldehyde tetramethyl acetal following the general procedure and purified by recrystallizing from acetic acid to give white solid; mp=243-244°C; [Found; C, 61.32; H, 3.74. $C_{15}H_{10}O_2Cl_2$ requires C, 61.43; H, 3.42%]; UV(CH_2Cl_2) λ 233 (ε_{max} =24210), 294 nm (ε=18970); ν_{max}(KBr) 2985, 2920, 1235, 1155, 1070 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2.2 (2H, dd, *J* 2.4, 0.94 Hz, -CH_2), 3.9 (1H, t, *J* 5 Hz, 12-H), 6.1 (1H, t, *J* 2.3 Hz, 6-H), 6.7-7.3 (6H, m, Ph); δ_C (62.9 MHz, $CDCl_3$) 25.8 (12-C), 32.4 (13-C),

92.5 (6-C), 118.4, 126.2, 127.1 and 128.2 (aromatic C), 149.6 (=CO); *m/z* (EI) 293 (20, MH^+), 294 (33, MH^++1), 295 (7, MH^++2), 296 (5.1, MH^++3), 292 (49), 259 (13.4), 258 (8.1), 257(43), 168 (3.5), 167 (30.8), 166 (12.4), 165 (100), 102 (14), 101 (14.4), 63 (16), 43 (31%).

2,10-Dibromo-6,12-methano-12H-dibenzo[2,1-d:1′,2′-g][1,3]dioxocin (7f):

7f was obtained from **4f** and malonaldehyde tetramethyl acetal following the general procedure and purified by recrystallizing from acetic anhydride to give white solid; mp=264-265°C; [Found: C, 47.26; H, 2.97. $C_{15}H_{10}O_2Br_2$ requires C, 47.12; H, 2.62%]; UV(CH_2Cl_2)λ 241 (ε_{max}=29660), 293 nm(ε =28150); ν_{max}(KBr) 2980-2930, 1240, 1155, 1065 cm^{-1}. δ_H (250 MHz, $CDCl_3$) 2.18 (2H, dd, *J* 2.6, 0.85 Hz, -C<u>H</u>$_2$), 3.85 (1H, t, *J* 7.1 Hz, 12-<u>H</u>), 6 (1H, t, *J* 2 Hz, 6-<u>H</u>), 6.6-7.2 (6H, m, Ph) ; δ_C (62.9 MHz; $CDCl_3$) 25.31 (12-<u>C</u>), 32.4 (13-<u>C</u>), 92.5 (6-<u>C</u>), 114.1, 127.4, 130.5 and 131.3 (aromatic <u>C</u>), 149.5 (=<u>C</u>O); *m/z* (EI) 382 (82.9, MH^+), 383 (25, MH^++1), 384 (42, MH^++2), 385 (6, MH^++3), 304 (11.4), 303 (54), 302 (12), 301(54), 212 (10.5), 211 (98), 210 (14), 209 (100), 165 (26), 130 (43), 102 (39), 82 (25), 63 (49), 50 (26.5%).

8,16-Methano-16H-dinaphtho[2,1-d:1′,2′-g][1,3]dioxocin (3):

This compound has been obtained from the reaction of 2-naphthol with malonaldehyde tetramethyl acetal following the general procedure and purified by recrystallizing from acetic acid to give white solid; 88% yield; mp=236-237°C; [Found: C, 85.12; H, 5.08. $C_{23}H_{16}O_2$ requires C, 85.2; H, 5%]; ν_{max} (KBr) 2990-2900, 1240, 1165, 1070 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 5.4 (1H, t, *J* 2.95 Hz, 16-<u>H</u>), 6.25 (1H, t, *J* 2 Hz, 8-<u>H</u>), 2.45 (2H, dd, *J* 2 , 0.95 Hz, -C<u>H</u>$_2$), 7.1-8.45 (12H, m, Ph); *m/z* 324 (36, MH^+), 281 (52.6), 168 (62.4), 43 (78%).

2,10-Dimethyl-6,12-methano-12H-dibenzo [2,1-d:1′,2′-g][1,3]dithiocin (11):

This compound has been obtained from the reaction of *p*-thiocresol with malonaldehyde tetramethyl acetal.The procedure was essentially the same as for (**7a-f**). **11** has been separated from the solid mixture containing **12** by solubility in boiling petroleum ether . Dissolved part has been cooled and **11** has obtained and purified by recrystallizing from petroleum ether to give white solid; 25% yield; mp=148-149°C; [Found: C, 71.74; H, 5.58. $C_{17}H_{16}S_2$ requires C, 71.83; H, 5.63%]; UV(CH_2Cl_2)λ 254 (ε_{max}=23600), 233 nm (ε=16090); ν_{max} (KBr) 1220, 1165, 1150, 1060 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2 (6H, s, C<u>H</u>$_3$), 2.19 (2H, dd, *J* 3.8, 1.8 Hz, -C<u>H</u>$_2$), 2.64 (1H, t, *J* 9.4 Hz, 12-<u>H</u>), 4.25 (1H, t, *J* 7.64 Hz, 6-<u>H</u>), 6.7-7 (6H, m, Ph); δ_C (62.9 MHz, $CDCl_3$) 25.1 (<u>C</u>H$_3$), 35.3 (12-<u>C</u>), 41.2 (13-<u>C</u>), 85.9 (6-<u>C</u>), 130.8,131.5, 132.6, 135.3 and 137.54 (aromatic <u>C</u>), 140.2 (=<u>C</u>S); *m/z* (EI) 161 (34.6), 136 (100), 129 (1.5%).

2-3 H-benzo [2,1-b]thio pyranyl phenyl sulfide (12):

This compound has been obtained from the reaction of *P*-thiocresol with malonaldehyde tetramethyl acetal. In above experiment the insoluble part has been boiled in petroleum ether to remove the remained **11** and **12** has been purified to give white solid; 14% yield; mp=102-104°C ; ν_{max}(KBr) 1180, 1165, 1080 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2 (6H, m, -C<u>H</u>$_3$), 4.03 (1H, d, *J* 7.8 Hz, 7-<u>H</u>), 5.28 (2H, m, 13-<u>H</u>, 14-<u>H</u>), 7-7.2 (7H, m, Ph); *m/z* (EI) 284 (100, MH^+), 251 (16.5), 161 (38.4), 129 (1.5%).

8,16-Methano-16H-dinaphtho[2,1-d:1′,2′-g][1,3]dioxocin-2,14-diol (8):

2,7-Dihydroxynaphthalene (1.6g, 10 mmol), malonaldehyde tetramethyl acetal (1.6 mL, 10 mmol) and trifluoroacetic acid (10 mL) was allowed under stirring to stand at room temperature for 24h.The reation mixture was solidified. After addition of (15) mL of acetic acid, the product was collected by filtration and washed with water several times. Once recrystallization from ethanol-water (5/1,v/v) mixture to give (**8**). 81% yield; mp=306°C(dec); [**Found**: C, 77.15; H, 4.61. $C_{23}H_{16}O_4$ requires C, 77.53; H, 4.5%]; UV(EtOH)λ 231 nm (ε_{max}=29300); ν_{max}(KBr) 3400-3250 (br), 2990-2910, 1240, 1150, 1075 cm^{-1}; δ_H (250 MHz, DMSO-d_6) 2.2 (2H, dd, *J* 3, 1.8 Hz, -C<u>H</u>$_2$), 5.2 (1H, t, *J* 2.95 Hz,16-<u>H</u>), 6.4 (1H, t, *J* 2 Hz, **8**-<u>H</u>), 6.8-7.9 (10H, m, Ph), 9.2 (2H, s, -O<u>H</u>); *m/z* (EI) 356 (30, MH^+), 340 (6.1), 339 (6.1), 197 (100), 184 (15.1), 181 (14), 168 (15), 160 (13.8), 139 (13), 115 (12), 77 (13), 43 (39%).

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