5a,10b-Dihydrobenzofuro[2,3-b]benzofuran Type Compounds and Related Products from *p*-Substituted Phenols and Glyoxal

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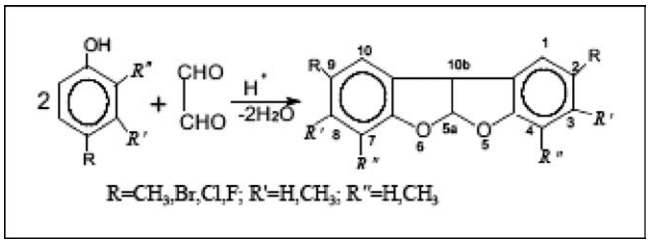

Condensation reactions of glyoxal with *p*-substituted phenol derivatives **1a–f** have been carried out and the corresponding 5a,10b-dihydrobenzofuro[2,3-b]benzofuran **4a–f** type compounds were obtained in good to excellent yields. The resulting dimeric products carrying methyl groups **4a–d** were converted to the corresponding carboxylic acid derivatives as the new polymer forming monomers. Many of these reactions gave novel structures. No definite product was obtained by the similar reactions of glyoxal with thiophenol and aniline in place of phenols.

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INTRODUCTION

Some of dialdehydes and especially their synthetic equivalents are interesting reactive precursors in organic chemistry and are regarded as useful starting material for the preparation of the thermally stable polymers [1–9]. Condensation of unsubstituted phenols with glyoxal bisulfite or glyoxal has been reported to produce insoluble resins [10]. The reaction of 2-naphthol with glyoxal has been reported by Dischendorfer and assigned the reaction product after alkaline fusion as structure **5** with a benzofurobenzofuran moiety in its structure [8]. The preparation of novel aromatic compounds with one or two dihydrofurofuran moieties starting from 2-naphthol and glyoxal has been reported [11].

Recently, we have reported the possibility of using trifluoroacetic acid as suitable medium for the condensation of *p*-substituted phenolic compounds with malonaldehydetetramethyl acetal as very reactive protected dialdehyde [12]. In this context, we have also reported the synthesis of 1,1,4,4–tetrakis (2-hydroxyphenyl)butane type compounds from the condensation of phenols with 2,5-dimethoxytetrahydrofuran using trifluoroacetic acid as both solvent and catalyst [13]. In our previous studies, condensation reaction of *p*-substituted phenols with glutaraldehyde bisulfite in the presence of trifluoroacetic acid as both solvent and catalyst and formation of propano-dibenzo [2, 1 − *d* : 1′, 2′ −*g*] [1,3] dioxocin type compounds were reported [14].

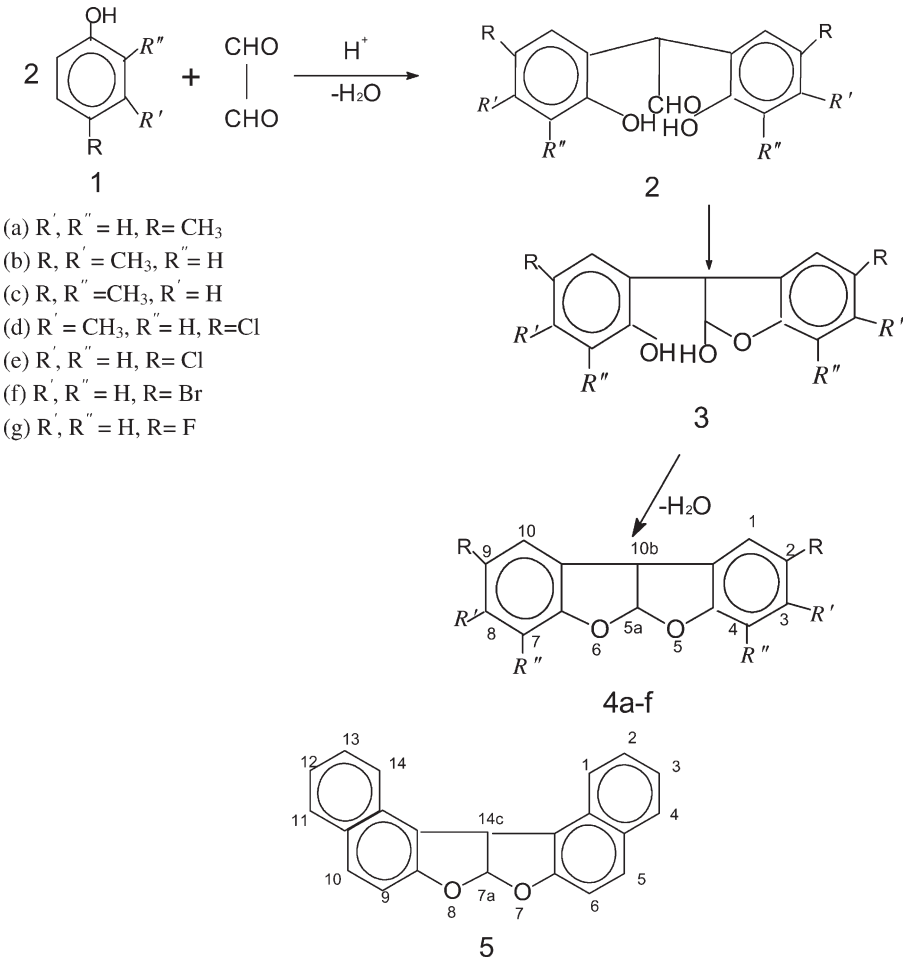
Condensation of 2-naphthol with glyoxal bisulfite in the presence of formic acid at 50–60°C has been shown to give dimeric product, namely 7a,14c-dihydronaphtho[2,1-b] naphtha [2′, 1′ : 5,6] furo[3,2-d] furan in only 22% yield [15]. The base catalyzed reaction of 2-naphthol with glyoxal was also investigated in which the final product was considered to be similar to that obtained from the acid catalyzed reaction [16–18].To the best of our knowledge, condensation reaction of *p*-substituted phenols with glyoxal has not been exploited for polymer forming monomers. However, the yield of formation of dimeric products was low and not enough for further transformations when we used sulphuric acid and formic acid as condensing agent [5,15,19].

To increase the yield in dimeric product and to examine more accurately the experimental conditions for the condensation reaction of *p*-substituted phenols and 2-naphthol with glyoxal and also in continuation of our research on the synthesis of thermally stable polymers from polymerisable monomers [20], we have also studied synthetic routes towards 5a,10b-dihydrobenzofuro[2,3-b]benzofuran type compounds as new model compounds and their related derivatives having suitable functional groups(e.g., dicarboxylicacid, dianhydride) which can be used as important monomers for the preparation of a variety of thermally stable polymers.

RESULTS AND DISCUSSION

To study the possibility of using the reported method for condensation of 2-naphthol and glyxoalbisulfite with

Scheme 1



different phenols, we performed the reaction of phenols with glyoxalbisulfite under the reported conditions [15]. It was observed that this method cannot work for phenolic compounds. These observations led us to design another applied synthetic method for the condensation of *p*-substituted phenolic compounds with glyoxal. The possibility of condensation of different phenols with glyoxal bisulfite in acetic acid in the presence of sulfuric acid as catalyst were studied. Condensation of phenols with glyoxal bisulfite occurred and the corresponding 5a,10b-dihydrobenzofuro[2,3-b]benzofuran type compounds (**4a–f**) were obtained in low to moderate yields. To increase the yields of the products, we tried the same reactions using glyoxal solution in the presence of methane sulphonic acid as catalyst. The reaction of phenols carrying alkyl groups (**1a–c**) or having both alkyl and halogen (**4d**) gave excellent yields of their corresponding 5a,10b-dihydrobenzofuro [2, 3-b]benzofuran (**4a–f**). The reaction of phenols carrying only halogens (**1e,f**) gave moderate yields (Scheme 1).

For the study of structure–reactivity relationship, the reaction of *p*-substituted phenols having electron withdrawing substituents such as **1g** and 2,4-dichlorophenol with glyoxal under the same reaction condition was also investigated. No dimeric products as structure **4** with a benzofuro-benzofuran moiety (acetal type structure) in their structures were detected (Scheme 1). The results with the structurally different *p*-substituted phenolic compounds are shown in the Table 1.

It was found that the electron withdrawing groups retard the reaction and the electron donating substituents such as methyl were favorable in the reaction. These observations are in good agreement with the suggested mechanism as shown in Scheme 1.

We next decided to produce the dimeric product similar to that of **4a–f** but with sulfur or nitrogen in place of oxygen in the furan rings. However, we were not successful in using a similar reaction of glyoxal and thiophenols and/or aniline in place of phenols to reach our objective. No definite product was obtained by the reactions. When we treated glyoxal with aniline, for example, the expected product, a dihydroindole ring, was never produced. As is well-known, an amine and an aldehyde always react to produce a schiff base as a classical reaction.

Table 1

Reaction of phenolic compounds (**1a–f**) and 2-naphthol with glyoxal.

Substrate	Method of preparation[a]	Reaction time (h)	Product (yield/%)[b]
2-naphthol	A	1	**5** (81)
	B	1.5	**5** (51)
1a	A	1	**4a** (86)
	B	1.5	**4a** (53)
1b	A	1	**4b** (83)
	B	2.5	**4b** (54)
1c	A	1	**4c** (81)
	B	2.5	**4c** (52)
1d	A	1.5	**4d** (80)
	B	2	**4d** (50)
1e	A	1.5	**4e** (28)
	B	4	**4e** (8)
1f	A	2	**4f** (29)
	B	5	**4f** (7)
1g	A	2	[c]
	B	4	–

[a] A: glyoxal in CH_3SO_3H; B: glyoxalbisulfite in H_2SO_4.
[b] Yields refer to isolated products.
[c] No reaction.

Condensation of 2 moles of phenols (**1a–f**) with glyoxal solution and bisulfite occurs first through Friedel-Crafts reaction (one carbonyl group) to give **2** followed by an intramolecular acetalization reaction as suggested for the condensation of phenols with malonaldehyde tetramethyl acetal, 2,5-dimethoxytetrahydrofuran and glutaraldehyde [12–14], (Scheme 1).

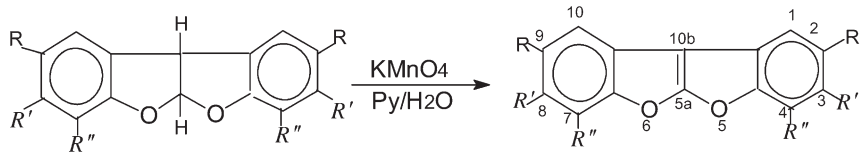
The structure of all compounds **4a–f, 5** were deduced from their IR, ^{1}H, ^{13}C-NMR and mass spectral data. The IR spectra show no carbonyl and hydroxyl groups. In all cases, the ^{1}H-NMR spectra indicated that the compounds had the acetal structure. The spectra of all these compounds showed a doublet (J = 6–7 Hz) in the region δ 4.8–5.82 (assigned to the hydrogen on the diarylmethyl carbon (10b-H), (14c-H) and a doublet (J = 6–7 Hz) in the region δ 6.8–7 ppm assigned to the hydrogen on the acetal carbon (5a-H), (7a-H). The ^{13}C-NMR spectra show two aliphatic resonances for the diaryl methyl (10b-C, 14C) in the region δ 48–50.85 and acetal carbons (5a-C, 7a-C) at region δ 111–112.4 ppm respectively, consistent with the overall mirror symmetry. In all of these compounds (**4a–f**,**5**) bands arising from the aromatic protons partially overlapped the doublet assigned to the hydrogen on the acetal carbon. It was found that, by expanding the NMR spectra in the aromatic region, the acetal hydrogen doublet was clearly separated from the bands attributed to the aromatic protons, and that overlapping was removed.

In conclusion, the simplicity of this method, good to excellent yields, readily available starting materials and the possibility of applying this method to phenols and naphthols make this method very useful for this type of transformation in organic synthesis.

To prepare the polymer forming monomers from dimeric products having two and tetramethyl groups (**4a–d**), we performed the ordinary aromatic side chain oxidation reaction of **4a–d** using $KMnO_4$ in the next stage. It was observed that the resulting reaction products had structures different from to that of our expected and a surprising result was obtained. Spectral investigations showed that aromatization had occurred in the products (**6a–d**) in addition to oxidation of the methyl groups as shown in Scheme 2.

The IR spectra of the compounds **6a–d** showed broad absorption bands around 2530–3500 (acidic H,s) and the acidic C=O stretching absorption in the region 1680–1715 cm^{-1}, confirming the presence of carboxylic acid groups in the structures. The ^{1}H-NMR spectra showed no peaks associated with methyl groups and no doublets around 4.88–4.92 ppm for diaryl methyl protons (10b). There appeared only a complicated collection of peaks around the aromatic hydrogen region in the ^{1}H-NMR spectra of the products. In other words, using $KMnO_4$ as an oxidizing agent causes a dehydrogenation reaction on 5a and 10b hydrogens which leads to the production of diacids **6a**, **6d** and tetra acids **6a**, **6c**, respectively. The tetra acid (**6b**) did not melt, but it underwent thermal

Scheme 2



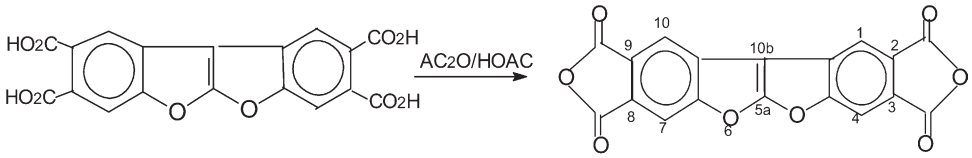
4

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

6

a) R′,R″ =H, R = CO_2H
b) R, R′= CO_2H, R″ =H
c) R, R″ = CO_2H , R′ = H
d) R′ =CO_2H, R"= H, R = Cl

Scheme 3



6b **7**

cyclodehydration to the dianhydride. The ^{1}H-NMR also show a peak in the region 12.8–13 ppm assigned to the acidic protons.

All the evidence, ie., no peaks for the 10b and 5a hydrogens in ^{1}H-NMR spectra and a twofold difference between our expected molecular weights and that of experimental results in GC-MS, led us to the conclusion that the exact structures for the oxidation reaction products must be as structures **6a–d**, a series of molecules with fully aromatic structures (Scheme 2).

Finally, the dianhydride (**7**) was prepared by dehydration of the tetra acid (**6a**) in acetic acid and acetic anhydride (Scheme 3).

After compound **6b** was dehydrated into dianhydride **7**, the absorption bands of O—H and C=O stretching disappeared and the characteristic absorptions of the C=O groups in cyclic anhydride were observed at 1851 (asymmetric stretching) and 1782 (symmetric stretching) cm^{-1}, hence confirming the presence of an anhydride ring in the structure. The ^{1}H-NMR spectrum of dianhydride (**7**) showed no acidic protons, and the remaining protons were only aromatic hydrogens. The mass spectral data completed the structural confirmation of dianhydride **7** in which the peak appeared at m/z 348 (MH^+, 100%)

In conclusion, we successfully prepared a series of new wholly aromatic polymer forming monomers from a relatively cheap raw material and through a high yield route, that involves the use of common, in expensive reagents. Specially, because of their complete aromatic structures, these monomers may be the good candidates in the synthesis of several types of heat stable polymers such as polyimide, polyamide, polyesters, polybenzimidazoles, etc. Synthesis and study of the corresponding polymers derived from the diacids (**6a**, **6d**) and dianhydride (**7**) and the preparation of their derivatives having several types of functional groups, to reach some kinds of polymers are underway and the results will be reported soon.

EXPERIMENTAL

Materials and instruments. 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 and FTIR spectra were recorded using a Perkin–Elmer 781 and Unicam Matteson 1000 spectrometers, respectively. UV spectra were recorded on a Pharmacia biotech ultra spec 3000 model 80-2106-20 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a 250 MHz Bruker Avance DPX-250 and 400 MHz Bruker spectrometers using tetramethyl silane (TMS) as an internal standard at 25°C with frequencies of 400, 250, and 62.9 MHz for the ^{1}H and ^{13}C spectra, respectively. Mass spectra were recorded under electron impact at 70eV on a shimadzu GCMS-QP1000 Ex instrument. Elemental analysis was performed by RIPI.

Glyoxal bisulfite. To a solution of sodium bisulfite (30%) was added glyoxal in 2/1 mole ratio at room temperature. The bisulfite adduct was precipitated by addition of ethanol to the solution and dried *in vacuo* at 60°C.

General procedures for (4a–f). ***Method A.*** To a 500 mL round bottomed flask was charged with phenolic compound (**1a–f**) (0.10 mol) glyoxal, (0.05 mol of a 30% aqueous solution) and acetic acid (100 mL). The mixture was dissolved in acetic acid. Methane sulphonic acid (25–30 mL) was added drop by drop, with stirring, the temperature of the reaction mixture being kept between 30 and 35°C. During the addition of the methane sulphonic acid (20–50 min) the acetal began to precipitate from solution. The mixture was then stirred at 30–35°C until the total time of addition and stirring 1–2 h. The cooled reaction mixture was then poured into water (500 mL), and the crude product was collected by filtration and wash with water and ethanol. Details concerning the purification of each individual reaction product are given under the appropriate title in the following part of the experimental.

Method B. In a fume cupboard, to a 500 mL round bottomed flask with a hot water bath H_2O (150 mL), acetic acid (70 mL), glyoxal bisulfite(13 g, 0.05 mol) and phenolic compounds (**1a–f**) (0.1 mol) were added. The glyoxalbisulfite was dissolved upon stirring and increasing the temperature. After the temperature reached 80°C, concentrated sulfuric acid (40–45 mL) was added drop by drop and the temperature of the reaction mixture was kept between 85 and 90°C. During the addition of sulfuric acid (40–60 min) the reaction product began to precipitate from solution. The mixture was then stirred at 85–90°C until the total time of addition and stirring was 1.5–4 h. The cooled reaction mixture was filtered and the crude product was then poured into water (500 mL), collected by filtration and washed with water and ethanol. Reaction products were purified by appropriate methods specified below.

2,9-Dimethyl-5a,10b-dihydrobenzofuro[2,3-b]benzofuran (4a). 4a was obtained from **1a** and glyoxal following the general procedure and purified by recrystallizing from ethanol to give white solid; mp = 195–196°C(lit., 195°C, [6]); [Found: C, 80.50;

H, 5.84 $C_{16}H_{14}O_2$ requires C,80.67; H,5.88%]; UV(CH_2Cl_2) λ 293.3 (ε_{max} = 32440), 234.5 (ε_{max} = 18940) ν_{max} (KBr) 2820–3030, 1245, 1185, 1000 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2.31 (6*H,s*, *CH*$_3$), 4.81(1H, d, *J* 6.46 Hz, 10b-*H*), 6.81(1H, d, *J* 6.50 Hz, 5a-*H*), 6.61–7.20 (6H, m, Ar*H*); δ_C (62.9 MHz, $CDCl_3$)19.40 (*C*H$_3$), 50.10(10b-*C*), 111.60 (5a-*C*), 118.71, 122.65, 127.45, 131.65, 133.42(aromatic*C*), 157.05(=*C*O); m/z (EI) 238(100, MH^+), 195 (39.4), 165(18.1%)

2,3,8,9-Tetramethyl-5a,10b-dihydrobenzofuro[2,3-b]benzofuran (4b). 4b was obtained from **1b** and glyoxal following the general procedure and purified by recrystallizing from ethanol or acetic acid to give white solid; mp = 233–234°C; [Found: C, 81.16; H, 6.78 C_{18} H_{18} O_2 requires C, 81.20; H, 6.76%]; UV (CH_2Cl_2) λ 295.3 (ε_{max} = 31140), 237.5 (ε_{max} = 14940); ν_{max} (KBr) 3010–2900, 1260, 1160, 1055, 1000 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2.165 (6*H, s* − *CH*$_3$), 2.18 (6*H, s* − *CH*$_3$), 4.88(1H, d, *J* 6.45 Hz, 10b*H*), 6.81(1H,d, *J* 6.48 Hz, 5a-*H*), 6.67(2H, s, Ar*H*), 7.10(2H, s, Ar*H*); δ_C (62.9MHz, $CDCl_3$)19.38, and 20.06 (*CH*$_3$), 50.20(10b–C),111.57(5a-*C*), 112.99, 124.56, 124.72, 130.18, 137.39(aromatic*C*), 156.03(=*C*O); m/z(EI)266 (100,MH^+), 251(16.3), 223(15.1), 208(29), 179(4.8), 165(5.3), 118(47), 69(45), 55(29), 40(100%).

2,4,7,9-Tetramethyl-5a,10b-dihydrobenzofuro[2,3-b]benzofuran (4c). (**4c**) was obtained from **1c** and glyoxal following the general procedure and purified by refluxing in ethanol and recrystallizing from acetic acid to give white solid; mp = 206–207°C(lit., 206°C, [6]); [Found: C, 81.19; H, 6.81. $C_{18}H_{18}O_2$ requires C, 81.20; H, 6.76%]; UV (CH_2Cl_2) 293.8 (ε_{max} = 27,080), 233.7 (ε_{max} = 28,200); ν_{max}(KBr)3000-2900, 1210, 1135, 1075, 975 cm^{-1}; δ_H(250MHz, $CDCl_3$) 2.23(6H, s,C*H*, 2.28(6H, s, *CH*$_3$), 4.91(1H, d, *J* 6.47 Hz, 10b-*H*), 6.86(1H, d, *J* 6.71Hz, 5a-*H*), 6.78 (2H, s, Ar*H*), 7.01(2H, s, Ar*H*); δ_c (62.9 MHz, $CDCl_3$) 15.03 and 20.77(*C*H$_3$), 50.85(10b-*C*), 111.80 (5a-*C*),19.81, 121.65, 126.61, 130.77, 132.45 (aromatic*C*),154.13(=*C*O); m/z(EI) 266 (100, MH^+), 251(39), 223(25.1), 179(14.8), 165(15.2) 118(52), 69(42), 55(22), 40(100%).

2,9-Dichloro-3,8-dimethyl-5a,10b-dihydrobenzofuro[2,3-b]benzofuran (4d). 4d was obtained from **1d** and glyoxal following the general procedure except that only 0.1 mole of glyoxal (rather than 0.05 mole) was used and purified by recrystallizing from acetic acid or tetrahydrofuran to give white solid; mp = 255–256 °C; [Found: C, 62.46; H, 3.76. C_{16} $H_{12}Cl_2O_2$ requires C,62.54; H,3.908%]; UV (CH_2 Cl_2) λ 298.6(ε_{max} =12720), λ237.3(ε_{max} = 1040); ν_{max} (KBr)2990-2900, 1245, 1120, 1015, 975 cm^{-1}; δ_H (250 MHz,$CDCl_3$) 2.29(6*H,s*, *CH*$_3$), 4.92(1H, d, *J* 6.42Hz,10b-*H*, 6.86(1H, d, *J* 6Hz, 5a-*H*, 6.76 (2H, s,Ar*H*,7.29 (2H, s, Ar*H*); δ_c (62.9MHz,$CDCl_3$) 20.48(*C*H$_3$), 49.81 (10b-*C*), 112.39(5a-*C*),113.33, 125.84, 126.9, 129.87, 137.02 (aromatic*C*), 156.46(=*C*O); m/z (EI) 307(22.9, MH^+),308(65.1, MH^++1), 309(9.90, MH^++2), 310(9, MH^++3), 306(100), 271(30.4), 243 (35.2), 208 (14.8), 180(10.5), 179(15.4), 165(22.6), 76(28.3), 51(50.9%).

2,9-Dichloro-5a,10b-dihydrobenzofuro[2,3-b]benzofuran (4e). 4e was obtained from **1e** and glyoxal following the general procedure, except that only 0.1 mole of glyoxal(rather than 0.05 mole)was used and purified by recrystallizing from acetic acid to give white solid; mp = 233–234°C (lit., 233–234°C, [5,6]); [Found: C, 60.10; H, 2.69. $C_{14}H_8Cl_2O_2$ requires C, 60.215; H, 2.867%]; UV (CH_2Cl_2) λ 298.6 (ε_{max} = 17400), 233(ε_{max} =24110); ν_{max} (KBr) 2970, 1235, 1105, 1065, 975 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 4.91 (1H, d, *J* 6.43Hz,10b-*H*), 6.48 (1H, d, *J* 6.73 Hz, 5a-*H*), 6.73–7.30 (6H, m, Ar*H*); m/z (EI) 278 (100, MH^+), 279 (14, MH^++1) 280(65.8, MH^++2), 243(28.8), 215(84.9), 217(26), 197(13.7), 169(53.4) 152(63), 89(28.8), 75(53.4), 63(57.5%).

2,9-Dibromo-5a,10b-dihydrobenzofuro[2,3-b]benzofuran (4f). 4f was obtained from **1f** and glyoxal following the general procedure, except that only 0.1 mole of glyoxal(rather than 0.05 mole)was used and purified by refluxing in ethanol and recrystallizing from acetic acid to give white solid; mp = 255–256°C, [Found: C, 44.30; H,2.18. $C_{14}H_8$ Br_2O_2 requires C, 45.652; H, 2.174%]; UV(CH_2Cl_2) λ 298 (ε_{max} = 29150), 244 (ε_{max} = 28660); ν_{max} (KBr) 2955, 1230, 1105, 1025, 985 cm^{-1}; δ_H(250 MHz, $CDCl_3$), 4.93(1H, d, *J* 7Hz, 10b-*H*, 6.82(1H, d, *J* 6.56Hz, 5a-*H*, 7.19–7.40 (6 H, m, Ar*H*; m/z (EI) 368(67.1, MH^+), 369 (9, *MH*$^+$ + 1), 370(32.1, MH^++2), 371(2.6, MH^++3), 366(33.8), 289(10.7), 287(10.3), 261(23.9), 259(25.2), 208(28.6), 180(44), 152(63.2), 134(20.1), 89(39.7), 76(73.5), 63 (100%).

7a,14c-Dihydronaphtho[2,1-b]naphtho[2′,1′:5,6]furo[3,2-d]furan (5). This compound has been obtained from the reaction of 2-naphthol with glyoxal following the general procedure and purified by recrystallizing from acetic acid or acetone to give white solid; mp = 236–237°C (lit., 236–237°C, [15,6]); [Found; C; 85.13; H,4.60. $C_{22}H_{14}O_2$ requires C, 85.14; H, 4.55%]; ν_{max} (KBr)845,805,735 cm^{-1}; δ_H (250 MHz, DMSO-d_6) 5.82 (1H, d, *J* 6 Hz, 14c-*H*), 7.20–8.40 (13H, m, ArH + 7a-*H*); δ_c (62.9 MHz, DMSO-d_6) 48.5 (d, 14c-*C*), 111.5, 114.4, 118.6, 122.9, 123.3, 126.4, 128.7, 129.5, 129.7, 130.1, 155.6 (aromatic *C*+7a-*C*); m/z (EI) 310(100, MH^+), 281(39%).

General procedure for 6a–d. A two-necked round bottomed flask with an effective stirrer, was charged with a solution of **6a–d** (0.032 mol) in a mixture of pyridine (200 mL) and water (100 mL). The temperature was elevated to near refluxing and $KMnO_4$ (0.29–0.58 mol) was added in small portions. Refluxing was continued for 8–24 h. After cooling to room temperature, the mixture was filtered and the residual MnO_2 was washed thoroughly with boiling water. The combined filtrates in an ice-water bath were acidified with hydrochloric acid. The white solid precipitate was filtered off, washed several times with water, and dried to afford **6a–d**. The products were purified by appropriate methods specified below.

Benzofuro [2,3-b]benzofuran-2,3,8,10tetracarboxylic dianhydride(7). In a 500 mL round bottomed flask, 8.7 g (0.025 mol) of tetra acid **6b** was suspended in 100 mL of glacial acetic acid and 200 mL of acetic anhydride. The mixture was boiled under reflux for 4h. Then, the mixture was filtered and left to crystallized overnight. The precipitated product was filtered out, washed with dry toluene, and dried to give white solid in 86% yield; [Found: C, 61.891; H,1.11. $C_{18}H_4O_8$ requires C, 62.08; H, 1.10%]; ν_{max} (KBr) 3125, 3051, 1858 (asym. C=O str.), 1780 (sym. C=O str.), 1629, 1439, 1185, 1152, 1130, 885 (C—O str.) cm^{-1}; δ_H (250MHz, DMSO-d_6) 8.78-8.32(s, 4H, Ar).

Benzofuro[2,3-b]benzofuran-2,9-dicarboxylic acid (6a). 6a was obtained from oxidation of **4a** with $KMnO_4$ (45.82g) in a 2:1 (v/v) pyridine: water mixture by heating to gentle reflux for 8h, following the general procedure and purified by recrystallizing from dilute ethanol to give white solid in 81 %yield; mp>300°C (lit. [19]); ν_{max}(KBr) 3500-2800, 1680 (C=O str.), 1450, 1237, 1157 cm^{-1}; δ_H (400MHz, DMSO-d_6) 12.92(2H,

s,-O*H*), 6.8–8.20(6H, m, Ar*H*); m/z (EI) 296(100, MH^+), 269(45.8), 241(75.1%);

Benzofuro[2,3-b]benzofuran-2,3,8,9-tetracarboxylic acid (6b). 6b was obtained from oxidation of **4b** with $KMnO_4$ (91.649) in a 2:1 (v/v) pyridine: water mixture by heating to gentle reflux for 24h, following the general procedure and purified by recrystallizing from a mixture of ethanol/water(2:1 v/v) to give white solid in 82% yield; mp>300°C;[Found: C, 55.89; H, 2.791. $C_{18}H_8O_{10}$ requires C, 56.25; H, 2.783%], ν_{max} (KBr) 3445-2530, 1710(C═O str.), 1609, 1482, 1422(C─O str.), 1264 cm^{-1}; δ_H(400MHz, DMSO-d_6) 12.81(4H, s, ─O*H*), 6.80–8.80 (4H, m, Ar*H*); m/z (EI) 366(84.6), 348 (94.5), 322 (27.2), 304 (32.6), 276 (95.7), 232 (14.5), 204 (48.6), 148 (35.8), 116(21.2), 98(62. 4), 74(100), 44(77.7%).

Benzofuro[2,3-b]benzofuran–2,4,7,9-tetracarboxylic acid (6c). 6c was obtained from oxidation of **4c** with $KMnO_4$(91.64g) in a 2:1(v/v) pyridine : water mixture by heating to gentle reflux for 24 h, following the general procedure and purified by recrystallizing from mixture of DMF/water (2:1 v/v) to give white solid in 84% yield; mp > 300°C;[Found: C, 56.89;H, 2.61. C_{18} H_8 O_{10} requires C, 56.25; H, 2.783%]; ν_{max} (KBr) 3450-2530, 1715 (C═O str.), 1609, 1482, 1450, 1421(C─O str.), 1265 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 13(4H, s, ─O*H*), 6.80–8.80 (4H, m, Ar-*H*); m/z(EI) 384 (29.1, MH^+), 322(27), 294(23.9), 276(9.2), 266(15.9), 232(16.6), 204(41), 194(14.1), 166 (12.8), 98 (21), 79(100), 52(97%).

2,9-Dichloro-benzofuro[2,3-b]benzofuran-3,8-dicarboxylic acid(6d). 6d was obtained from oxidation of **4d** with $KMnO_4$ (55.4g) in a 2:1 (v/v) pyridine: water mixture by heating to gentle reflux for 12 h, following the general procedure and purified by recrystallizing from mixture of DMAc/water (2:1 v/v) to give white solid in 83% yield; mp>300 °C; [Found: C, 62.15; H, 3.32. $C_{16}H_{10}O_2Cl_2$ requires C, 62.95; H, 3.2787%]; ν_{max} (KBr) 3450-2800, 1695 (C═O str.), 1605, 1465, 1451,1425(C─O str.), 1240, 1145 cm^{-1}; δ_H(400MHz, DMSO-d6) 13(2H, s-O*H*), 6.85–8.35(4H, m, Ar*H*); m/z(EI)305 (81,MH^+), 306(19, MH^++1), 307(12.7, MH^++2), 308 (9.1, MH^++3), 261(100), 243(56), 217(41), 208(19), 180(29), 165(24), 76(32.2%).

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