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SUPPLEMENTARY MATERIAL TO

Synthesis, characterization and dyeing behaviour of heterocyclic acid dyes and mordant acid dyes on wool and silk fabrics

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ANALYTIC AND SPECTRAL DATA OF THE HETEROCYCLIC ACID DYES

*4-((5-(2-Butylbenzofuran-3-yl-carbonyl)-2-hydroxyphenyl)diazenyl)-5-hydroxynaphthalene-2,7-disulphonic acid (**E1**)*. Pinkish blue colour; Yield: 74 %; m.p.: 166–169 °C; *Rf* value: 0.72; Anal. Calcd. for $C_{29}H_{24}N_2O_{10}S_2$ (FW: 625): C, 55.76; H, 3.87; N, 4.48; S, 10.27 %. Found: C, 55.72; H, 3.84; N, 4.41; S, 10.24 %; IR (KBr, cm^{-1}): 3463 (–OH), 3072 (=CH, aromatic), 1628 (C=O, diaryl), 1521 (N=N), 1520 (naphthalene substitution), 1481 (C=C, aromatic), 1333 (C–N), 1101 (C–O), 1030, 650 (sulphonic acid), 732, 584, 481 (substituted benzene); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 0.90 (3H, *t*, $J_{H–H}$ = 8.0 Hz, $–CH_3$), 1.31–2.40 (6H, *m*, $–CH_2–$), 5.35 (2H, *s*, Ar–OH), 7.31–8.72 (4H, *m*, substituted naphthalene), 7.32–7.89 (7H, *m*, substituted benzofuran and benzene), 8.1 (2H, *s*, $–SO_3H$); ^{13}C-NMR (75 MHz, DMSO-d_6, δ / ppm): 120.8 (C_3) (=CH, benzofuran), 168.0 (C_2) (=CH, benzofuran), 31.6 (CH_2, butyl), 26.3 (CH_2, butyl), 19.9 (CH_2, butyl), 13.5 (CH_3, butyl), 190.7 (C_1, methanone), 156.1 (C_4, phenolic-OH), 158.7 (naphthol), 125.2 (C–N=N), 147.3 (N=N–C), C–Ph of benzofuran: 123.2 (C_1), 120.9 (C_2), 123.3 (C_3), 124.7 (C_4), 111.5 (C_5), 156.1 (C_6), O=C–Ph of benzene: 123.9 (C_1), 123.8 (C_2), 125.2 (C_3), 156.1 (C_4), 119.2 (C_5), 133.3 (C_6), –N=N–naphthyl: 147.3 (C_1), 116.0 (C_2), 128.3 (C_3), 141.3 (C_4), 117.4 (C_5), 141.8 (C_6), 106.2 (C_7), 158.7 (C_8), 119.4 (C_9), 129.5 (C_{10}).

*(*E*)-7-((5-(2-Butylbenzofuran-3-yl-carbonyl)-2-hydroxyphenyl)diazenyl)-4--hydroxynaphthalene-2-sulphonic acid (**E2**)*. Pinkish blue colour; Yield: 81 %; m.p.: 148–152 °C; *Rf* value: 0.79. Anal. Calcd. for $C_{29}H_{24}N_2O_7S$ (FW: 545): C, 63.96; H, 4.44; N, 5.14; S, 5.89 %. Found: C, 63.92; H, 4.38; N, 5.10; S, 5.86 %; IR (KBr, cm^{-1}): 3450 (–OH), 3082 (=CH, aromatic), 1624 (C=O, diaryl), 1540 (substituted naphthalene), 1522 (N=N), 1490 (C=C, aromatic), 1345 (C–N), 1101

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(C–O), 1032, 653 (sulphonic acid), 744, 564, 478 (substituted benzene); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 0.90 (3H, *t*, $J_{H–H}$ = 8.0 Hz, –CH_3), 1.31–2.40 (6H, *m*, –CH_2–), 5.35 (2H, *s*, Ar–OH), 7.31–8.72 (5H, *m*, substituted naphthalene), 7.32–7.89 (7H, *m*, substituted benzofuran and benzene), 8.2 (1H, *s*, –SO_3H); ^{13}C-NMR (75 MHz, DMSO-d_6, δ / ppm): 120.8 (C_3) (=CH, benzofuran), 168.0 (C_2) (=CH, benzofuran), 31.6 (CH_2, butyl), 26.3 (CH_2, butyl), 19.9 (CH_2, butyl), 13.4 (CH_3, butyl), 190.7 (C_1, methanone), 156.1 (C_4, phenolic-OH), 153.9 (naphthol), 125.2 (C–N=N), 151.4 (N=N–C), C–Ph of benzofuran: 123.2 (C_1), 120.9 (C_2), 123.3 (C_3), 124.7 (C_4), 111.5 (C_5), 156.1 (C_6), O=C–Ph of benzene: 123.9 (C_1), 123.8 (C_2), 125.2 (C_3), 156.1(C_4), 119.2 (C_5), 133.3 (C_6), –N=N–naphthyl: 151.4 (C_1), 117.6 (C_2), 121.8 (C_3), 153.9 (C_4), 106.1 (C_5), 141.2 (C_6), 118.1 (C_7), 130.9 (C_8), 133.9 (C_9), 128.7 (C_{10}).

*4-((5-(2-Butylbenzofuran-3-yl-carbonyl)-2-hydroxyphenyl)diazenyl)-5-hydroxynaphthalene-1,7-disulphonic acid (**E$_3$**)*. Reddish brown colour; Yield: 76 %; m.p.: 146–150 °C; *Rf* value: 0.79. Anal. Calcd. for $C_{29}H_{24}N_2O_{10}S_2$ (FW: 624): C, 55.76; H, 3.87; N, 4.48; S, 10.27 %. Found: C, 55.74; H, 3.81; N, 4.43; S, 10.24 %; IR (KBr, cm^{-1}): 3481 (–OH), 3070 (=CH, aromatic), 1632 (C=O, diaryl), 1542 (N=N), 1525 (substituted naphthalene), 1483 (C=C, aromatic), 1337 (C–N), 1103 (C–O), 1029, 650 (sulphonic acid), 737, 562, 472 (substituted benzene); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 0.90 (3H, *t*, $J_{H–H}$ = 8.0 Hz, –CH_3), 1.31–2.40 (6H, *m*, –CH_2–), 5.35 (2H, *s*, Ar–OH), 7.31–8.72 (4H, *m*, substituted naphthalene), 7.32–7.89 (7H, *m*, substituted benzofuran and benzene), 8.1 (2H, *s*, –SO_3H); ^{13}C-NMR (75 MHz, DMSO-d_6, δ / ppm): 120.8 (C_3) (=CH, benzofuran), 168.0 (C_2) (=CH, benzofuran), 31.6 (CH_2, butyl), 26.3 (CH_2, butyl), 19.9 (CH_2, butyl), 13.5 (CH_3, butyl), 190.7 (C_1, methanone), 156.1 (C_4, phenolic -OH), 158.7 (naphthol), 125.2 (C–N=N), 147.3 (N=N–C), C–Ph of benzofuran: 123.2 (C_1), 120.9 (C_2), 123.3 (C_3), 124.7 (C_4), 111.5 (C_5), 156.1 (C_6), O=C–Ph of benzene: 123.9(C_1), 123.8 (C_2), 125.2 (C_3), 156.1 (C_4), 119.2 (C_5), 133.3 (C_6), –N=N–naphthyl: 147.3 (C_1), 116.0 (C_2), 128.3 (C_3), 141.3 (C_4), 117.4 (C_5), 141.8 (C_6) , 106.2 (C_7), 158.7 (C_8), 119.4 (C_9), 129.5 (C_{10}).

*(*E*)-6-((5-(2-Butylbenzofuran-3-yl-carbonyl)-2-hydroxyphenyl)diazenyl)-naphthalene-2-sulphonic acid (**E$_4$**)*. Yellowish pink colour; Yield: 83 %; m.p.: 136–140 °C; *Rf* value: 0.81; Anal. Calcd. for $C_{29}H_{24}N_2O_6S$ (FW: 529): C, 65.90; H, 4.58; N, 5.30; S, 6.07 %. Found: C, 65.88; H, 4.52; N, 5.27; S, 6.02 %; IR (KBr, cm^{-1}): 3633 (–OH), 3080 (=CH, aromatic), 1652 (C=O, diaryl), 1560 (substituted naphthalene), 1532 (N=N), 1473 (C=C, aromatic), 1338 (C–N), 1104 (C–O), 1032, 653 (sulphonic acid), 782, 741, 583, 485 (substituted benzene); ^{1}H--NMR (400 MHz, DMSO-d_6, δ /ppm): 0.90 (3H, *t*, $J_{H–H}$ = 8.0 Hz, –CH_3), 1.31––2.40 (6H, *m*, –CH_2–), 5.35 (1H, *s*, Ar–OH), 7.31–8.72 (6H, *m*, substituted naphthalene), 7.32–7.89 (7H, *m*, substituted benzofuran and benzene), 8.2 (1H, *s*, –SO_3H); ^{13}C-NMR (75 MHz, DMSO-d_6, δ / ppm): 120.8 (C_3) (=CH, benzofu-

ran), 168 (C_2) (=CH, benzofuran), 31.6 (CH_2, butyl), 26.3 (CH_2, butyl), 19.9 (CH_2, butyl), 13.5 (CH_3, butyl), 190.7 (C_1, methanone), 156.1 (C_4, phenolic-OH), 125.2 (C–N=N), 151.3 (N=N–C), C–Ph of benzofuran: 123.2 (C_1), 120.9 (C_2), 123.3 (C_3), 124.7 (C_4), 111.5 (C_5), 156.1(C_6), O=C–Ph of benzene: 123.9 (C_1), 123.8 (C_2), 125.2 (C_3), 156.1 (C_4), 119.2 (C_5), 133.3 (C_6), –N=N–naphthyl: 151.3 (C_1), 120.8 (C_2), 127.3 (C_3), 125.8(C_4), 140.3 (C_5), 123.4 (C_6) , 129.6 (C_7) , 121.0 (C_8), 133.4 (C_9), 134.9 (C_{10}).

*(*E*)-2-((5-(2-Butylbenzofuran-3-yl-carbonyl)-2-hydroxyphenyl)diazenyl)-naphthalene-1-sulphonic acid (**E**$_5$).* Chocolate brown colour; Yield: 79 %; m.p.: 138–142 °C; *Rf* value: 0.80. Anal. Calcd. for $C_{29}H_{24}N_2O_6S$ (FW: 529): C, 65.90; H, 4.58; N, 5.30; S, 6.07 %. Found: C, 65.86; H, 4.49; N, 5.25; S, 6.01 %; IR (KBr, cm^{-1}): 3580 (–OH, phenolic), 3070 (=CH, aromatic), 1621 (C=O, diaryl), 1575 (substituted naphthalene), 1531 (N=N), 1482 (C=C, aromatic), 1463 (C–N), 1338 (C–O), 1034, 650 (sulphonic acid), 1103, 732, 574, 473 (substituted benzene); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 0.90 (3H, *t*, $J_{H–H}$ = 8.0 Hz, –CH_3), 1.31–2.40 (6H, *m*, –CH_2–), 5.35 (1H, *s*, Ar–OH), 7.31–8.72 (*m*, 6H, substituted naphthalene), 7.32–7.89 (7H, *m*, substituted benzofuran and benzene), 8.2 (1H, *s*, –SO_3H). ^{13}C-NMR (75 MHz, DMSO-d_6, δ / ppm): 120.8 (C_3) (=CH, benzofuran), 168 (C_2) (=CH, benzofuran), 31.6 (CH_2, butyl), 26.3 (CH_2, butyl), 19.9 (CH_2, butyl), 13.5 (CH_3, butyl), 190.8 (C_1, methanone), 156.2 (C_4, phenolic-OH), 125.3 (C–N=N), 151.7 (N=N–C), C–Ph of benzofuran: 123.4 (C_1), 120.9 (C_2), 123.6 (C_3), 124.5 (C_4), 111.7 (C_5), 156.3 (C_6), O=C–Ph of benzene: 123.8 (C_1), 123.9 (C_2), 125.4 (C_3), 156.6 (C_4), 119.8 (C_5), 133.3 (C_6), –N=N–naphthyl: 151.3 (C_1), 120.8 (C_2), 127.3 (C_3), 125.8(C_4), 140.3 (C_5), 123.4 (C_6), 129.6 (C_7), 121.2 (C_8), 133.4 (C_9), 134.9 (C_{10}).

*(*E*)-2-((5-(2-Butylbenzofuran-3-yl-carbonyl)-2-hydroxyphenyl)diazenyl)benzoic acid (**E**$_6$).* Red colour; Yield: 76 %; m.p.: 145–148 °C; *Rf* value: 0.83; Anal. Calcd. for $C_{26}H_{22}N_2O_5$ (FW: 442): C, 70.58; H, 5.01; N, 6.33 %. Found: C, 70.52; H, 4.88; N, 6.30 %; IR (KBr, cm^{-1}): 3430 (–OH, phenolic), 3540 (–OH, acidic), 3062 (=CH, aromatic), 1634 (C=O, diaryl), 1678 (C=O, carboxylic acid), 1581 (N=N), 1483 (C=C, aromatic), 1352 (C–N), 1103 (C–O), 1100, 850 (carboxylic acid), 783, 741, 583, 482 (substituted benzene); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 0.90 (3H, *t*, $J_{H–H}$ = 8.0 Hz, –CH_3), 1.31–2.40 (6H, *m*, –CH_2–), 5.35 (1H, *s*, Ar–OH), 7.32–8.41 (11H, *m*, substituted benzofuran and benzene), 11.0 (1H, *s*, –COOH); ^{13}C-NMR (75 MHz, DMSO-d_6, δ / ppm): 168.0 (C_2) (=CH, benzofuran), 120.8 (C_3) (=CH, benzofuran), 31.6 (CH_2, butyl), 26.3 (CH_2, butyl), 19.9 (CH_2, butyl), 13.5 (CH_3, butyl), 190.7 (C_1, methanone), 156.1 (C_4, phenolic-OH), 166.5 (–COOH), 125.2 (C–N=N), 154.1 (N=N–C), C–Ph of benzofuran: 123.2 (C_1), 120.9 (C_2), 123.3 (C_3), 124.7(C_4), 111.5 (C_5), 156.1(C_6), O=C–Ph of benzene: 123.9 (C_1), 123.8 (C_2), 125.2 (C_3), 156.1 (C_4), 119.2 (C_5),

133.3 (C_6), –N=N–Ph. of benzene: 154.1 (C_1), 122.9 (C_2), 134.2 (C_3), 127.8 (C_4), 127.2 (C_5), 117.0 (C_6).

*(*E*)-4-((5-(2-Butylbenzofuran-3-yl-carbonyl)-2-hydroxyphenyl)diazenyl)benzenesulphonic acid (**E**$_7$).* Red colour. Yield: 78 %; m.p.: 154–158 °C; *Rf* value: 0.83. Anal. Calcd. for $C_{25}H_{22}N_2O_6S$ (FW: 479): C, 62.75; H, 4.63; N, 5.85; S, 6.70 %. Found: C, 62.70; H, 4.58; N, 5.81; S, 6.67 %; IR (KBr, cm^{-1}): 3590 (–OH), 3063 (=CH, aromatic), 1632 (C=O, diaryl), 1533 (N=N), 1471 (C=C, aromatic), 1324 (C–N), 1103 (C–O), 1031, 652 (sulphonic acid), 780, 744, 586, 475 (substituted benzene); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 0.90 (3H, *t*, $J_{H–H}$ = 8.0 Hz, –CH_3), 1.31–2.40 (6H, *m*, –CH_2–), 5.35 (1H, *s*, Ar–OH), 7.32–8.41 (11H, *m*, substituted benzofuran and benzene), 8.2 (1H, *s*, –SO_3H); ^{13}C-NMR (75 MHz, DMSO-d_6, δ / ppm): 120.8 (C_3) (=CH, benzofuran), 168 (C_2) (=CH, benzofuran), 31.6 (CH_2, butyl), 26.3 (CH_2, butyl), 19.9 (CH_2, butyl), 13.5 (CH_3, butyl), 190.7 (C_1, methanone), 156.1 (C_4, phenolic-OH), 125.0 (C–N=N), 156.5 (N=N–C), C–Ph of benzofuran: 123.2 (C_1), 120.9 (C_2), 123.3 (C_3), 124.7 (C_4), 111.5 (C_5), 156.1(C_6), O=C–Ph of benzene: 123.9 (C_1), 123.8 (C_2), 125.2 (C_3), 156.1 (C_4), 119.2 (C_5), 133.3 (C_6), –N=N–Ph. of benzene: 156.5 (C_1), 124.3 (C_2), 123.2 (C_3), 147.7 (C_4), 123.2 (C_5), 124.3 (C_6).