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SUPPLEMENTARY MATERIAL TO

Optimization of electrochemical decolorization of certain arylazo pyridone dyes

JELENA M. MIRKOVIĆ[#], NEVENA Ž. PRLAINOVIĆ[#], GORDANA S. UŠĆUMLIĆ[#], BRANIMIR N. GRGUR and DUŠAN Ž. MIJIN*[#]

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11020 Belgrade, Serbia

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PHYSICAL, ANALYTIC AND SPECTRAL DATA FOR THE SYNTHESIZED DYES

*6-Hydroxy-1-(2-hydroxyethyl)-5-((4-methoxyphenyl)diazenyl)-4-methyl-2-oxo--1,2-dihydropyridine-3-carbonitrile (**1**).* Yield: 38 %; red orange powder; m.p.: 232.8–233.3 °C; Anal. Calcd. for $C_{16}H_{16}N_4O_4$: C, 58.53; H, 4.91; N, 17.06 %. Found: C, 58.35; H, 5.01; N, 16.95 %; IR (KBr, cm^{-1}): 3459 (N–H stretching of hydrazone unit), 2221 (–C≡N stretching of cyano group), 1667, 1630 (C=O stretching of carbonyl groups); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.50 (3H, *s*, CH_3), 3.54 (2H, *t*, *J* = 6.2 Hz, C**H**$_2$CH$_2$OH), 3.79 (3H, *s*, OCH_3), 3.94 (2H, *t*, *J* = 6.2 Hz, CH$_2$C**H**$_2$OH), 7.04 (2H, *d*, *J* = 9.0 Hz, Ar-H), 7.67 (2H, *d*, *J* = = 9.0 Hz, Ar-H), 14.75 (1H, *s*, NH hydrazone); ^{13}C-NMR (50 MHz, DMSO-d_6 δ / ppm): 160.9 (Py), 160.5 (Py), 159.1 (Py), 158.9 (Ar), 134.7 (Ar), 122.2 (Py), 119.4 (Ar), 115.6 (CN), 115.3 (Ar), 99.3 (Py), 57.6 (CH$_2$**C**H$_2$OH), 55.7 (OCH_3), 41.5 (**C**H$_2$CH$_2$OH), 16.4 (CH_3). UV–Vis (EtOH) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 460.0 (26360), 273.5 (6400).

*6-Hydroxy-1-(2-hydroxyethyl)-5-((4-hydroxyphenyl)diazenyl)-4-methyl-2-oxo--1,2-dihydropyridine-3-carbonitrile (**2**).* Yield: 45 %; red powder; m.p.: 272.2––272.4 °C; Anal. Calcd. for $C_{15}H_{14}N_4O_4$: C, 57.32; H, 4.49; N, 17.83 %. Found: C, 57.46; H, 4.58; N, 17.71 %. IR (KBr, cm^{-1}): 3494 (O–H stretching of hydroxy group, substituent), 2221 (–C≡N stretching of cyano group), 1661, 1618 (C=O stretching of carbonyl groups); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.50 (3H, *s*, CH_3), 3.54 (2H, *t*, *J* = 6.2 Hz, C**H**$_2$CH$_2$OH), 3.95 (2H, *t*, *J* = 6.2 Hz, CH$_2$C**H**$_2$OH), 4.82 (1H, *bs*, CH$_2$CH$_2$O**H**), 6.87 (2H, *d*, *J* = 9.0 Hz, Ar-H), 7.57 (2H, *d*, *J* = 9.0 Hz, Ar-H), 9.99 (1H, *s*, OH substituent), 14.84 (1H, *s*, NH hydrazone); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 161.0 (Py), 160.5 (Py),

* Corresponding author. E-mail: kavur@tmf.bg.ac.rs

159.0 (Py), 157.7 (Ar), 133.4 (Ar), 121.9 (Py), 119.7 (Ar), 116.6 (Ar), 115.8 (CN), 98.7 (Py), 57.7 (CH_2**C**H_2OH), 41.5 (**C**H_2CH_2OH), 16.4 (CH_3). UV–Vis (EtOH) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 466.5 (33280), 276.0 (8260).

*6-Hydroxy-1-(2-hydroxyethyl)-4-methyl-5-((4-nitrophenyl)diazenyl)-2-oxo-1,2--dihydropyridine-3-carbonitrile (**3**)*. Yield: 54 %; Yellow powder; m.p.: 279.6–280.4 °C; IR (KBr, cm^{-1}): 3467 (N–H stretching of hydrazone unit), 2227 (–C≡N stretching of cyano group), 1675, 1630 (C=O stretching of carbonyl groups); ^{1}H--NMR (200 MHz, DMSO-d_6, δ / ppm): 2.52 (3H, *s*, CH_3), 3.56 (2H, *t*, *J* = 6.2 Hz, C**H**$_2$$CH_2OH$), 3.94 (2H, *t*, *J* = 6.2 Hz, CH_2**CH**$_2$OH), 4.80 (1H, *bs*, CH_2CH_2O**H**), 7.90 (2H, *d*, *J* = 9.0 Hz, Ar-H), 8.29 (2H, *d*, *J* = 9.0 Hz, Ar-H), 14.32 (1H, *s*, NH hydrazone); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 160.5 (Py), 160.1 (Py), 159.3 (Py), 146.7 (Ar), 144.6 (Ar), 125.7 (Ar), 125.6 (Py), 117.8 (Ar), 114.8 (CN), 103.3 (Py), 57.5 (CH_2**C**H_2OH), 41.8 (**C**H_2CH_2OH), 16.6 (CH_3); UV–Vis (EtOH) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 429.0 (27360), 315.5 (8940), 270.0 (5320).

*6-Hydroxy-1-(2-hydroxyethyl)-4-methyl-2-oxo-5-(phenyldiazenyl)-1,2-dihydropyridine-3-carbonitrile (**4**)*. Yield: 48 %; yellow orange powder; m.p.: 227.2–227.8 °C; IR (KBr, cm^{-1}): 3447 (N–H stretching of hydrazone unit), 2225 (–C≡N stretching of cyano group), 1671, 1626 (C=O stretching of carbonyl groups); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.51 (3H, *s*, CH_3), 3.55 (2H, *t*, *J* = 6.2 Hz, C**H**$_2$$CH_2OH$), 3.94 (2H, *t*, *J* = 6.2 Hz, CH_2C**H**$_2$OH), 4.29 (1H, *bs*, CH_2CH_2O**H**), 7.28 (1H, *t*, *J* = 7.6 Hz, Ar-H), 7.47 (2H, *t*, *J* = 7.6 Hz, Ar-H), 7.69 (2H, *d*, *J* = 7.6 Hz, Ar-H), 14.54 (1H, *s*, NH hydrazone); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 160.9 (Py), 160.3 (Py), 159.3 (Py), 141.3 (Ar), 130.0 (Ar), 127.2 (Ar), 123.1 (Py), 117.6 (Ar), 115.3 (CN), 100.7 (Py), 57.6 (CH_2**C**H_2OH), 41.6 (**C**H_2CH_2OH), 16.5 (CH_3); UV–Vis (EtOH) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 428.5 (36340), 275.5 (7580).

*5-((4-Acetylphenyl)diazenyl)-6-hydroxy-1-(2-hydroxyethyl)-4-methyl-2-oxo--1,2-dihydropyridine-3-carbonitrile (**5**)*. Yield: 35 %; dark yellow powder; m.p.: 229.7–230.9 °C; Anal. Calcd. for $C_{17}H_{16}N_4O_4$: C, 59.99; H, 4.74; N, 16.46 %. Found: C, 59.84; H, 4.84; N, 16.57 %; IR (KBr, cm^{-1}): 3509 (N–H stretching of hydrazone unit), 2224 (–C≡N stretching of cyano group), 1679, 1636 (C=O stretching of carbonyl groups); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.51 (3H, *s*, CH_3 on heterocyclic), 2.56 (3H, *s*, $COCH_3$), 3.56 (2H, *t*, *J* = 6.0 Hz, C**H**$_2$$CH_2OH$), 3.94 (2H, *t*, *J* = 6.0 Hz, CH_2C**H**$_2$OH), 4.83 (1H, *bs*, CH_2CH_2O**H**), 7.78 (2H, *d*, *J* = 9.0 Hz, Ar-H), 8.02 (2H, *d*, *J* = 9.0 Hz, Ar-H), 14.41 (1H, *s*, NH hydrazone); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 196.8 ($COCH_3$), 160.6 (Py), 160.2 (Py), 159.3 (Py), 144.9 (Ar), 134.5 (Ar), 130.2 (Ar), 124.5 (Py), 117.3 (Ar), 115.0 (CN), 102.1 (Py), 57.6 (CH_2**C**H_2OH), 41.7 (**C**H_2CH_2OH), 26.8 ($COCH_3$), 16.6 (CH_3); UV–Vis (EtOH) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 439.0 (35420), 281.5 (9380).

*6-Hydroxy-1-(2-hydroxyethyl)-4-methyl-2-oxo-5-(p-tolyldiazenyl)-1,2-dihydropyridine-3-carbonitrile (**6**)*. Yield: 52 %; orange powder; m.p.: 231.2––231.9 °C; IR (KBr, cm^{-1}): 3420 (N–H stretching of hydrazone unit), 2223 (–C≡N stretching of cyano group), 1676, 1627 (C=O stretching of carbonyl groups); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.31 (3H, *s*, CH_3 substituent), 2.48 (3H, *s*, CH_3 on heterocyclic), 3.54 (2H, *t*, *J* = 6.2 Hz, C**H**$_2$CH$_2$OH), 3.93 (2H, *t*, *J* = 6.2 Hz, CH$_2$C**H**$_2$OH), 4.83 (1H, *bs*, CH$_2$CH$_2$O**H**), 7.26 (2H, *d*, *J* = 8.6 Hz, Ar-H), 7.56 (2H, *d*, *J* = 8.6 Hz, Ar-H), 14.59 (1H, *s*, NH hydrazone); ^{13}C--NMR (50 MHz, DMSO-d_6, δ / ppm): 160.9 (Py), 160.4 (Py), 159.2 (Py), 139.0 (Ar), 137.2 (Ar), 130.5 (Ar), 122.7 (Py), 117.6 (Ar), 115.4 (CN), 100.1 (Py), 57.6 (CH$_2$**C**H$_2$OH), 41.6 (**C**H$_2$CH$_2$OH), 20.9 (CH_3 substituent), 16.6 (CH_3 on heterocyclic); UV–Vis (EtOH) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 441.0 (37280), 277.5 (7960).

*4-((5-Cyano-2-hydroxy-1-(2-hydroxyethyl)-4-methyl-6-oxo-1,6-dihydropyridin--3-yl)diazenyl)benzoic acid (**7**)*. Yield: 41 %; yellow powder; m.p.: 289.8–290.9 °C. Anal. Calcd. for $C_{16}H_{14}N_4O_5$: C, 56.14; H, 4.12; N, 16.37 %. Found: C, 55.98; H, 4.23; N, 16.50 %; IR (KBr, cm^{-1}): 3410 (N–H stretching of hydrazone unit), 2227 (–C≡N stretching of cyano group), 1684, 1635 (C=O stretching of carbonyl groups); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.50 (3H, *s*, CH_3), 3.56 (2H, *t*, *J* = 6.2 Hz, C**H**$_2$CH$_2$OH), 3.94 (2H, *t*, *J* = 6.2 Hz, CH$_2$C**H**$_2$OH), 4.46 (1H, *bs*, CH$_2$CH$_2$O**H**), 7.72 (2H, *d*, *J* = 8.6 Hz, Ar-H), 7.96 (2H, *d*, *J* = 8.6 Hz, Ar-H), 12.90 (1H, *bs*, COOH), 14.39 (1H, *s*, NH hydrazone); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 166.8 (COOH), 160.7 (Py), 160.2 (Py), 159.3 (Py), 144.7 (Ar), 131.2 (Ar), 128.4 (Ar), 124.3 (Py), 117.3 (Ar), 115.1 (CN), 102.0 (Py), 57.6 (CH$_2$**C**H$_2$OH), 41.7 (**C**H$_2$CH$_2$OH), 16.6 (CH_3); UV–Vis (EtOH) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 433.0 (34940), 270.0 (8040).

*5-((4-Chlorophenyl)diazenyl)-6-hydroxy-1-(2-hydroxyethyl)-4-methyl-2-oxo--1,2-dihydropyridine-3-carbonitrile (**8**)*. Yield: 55 %; orange powder; m.p.: 246.8–247.2 °C; IR (KBr, cm^{-1}): 3447 (N–H stretching of hydrazone unit), 2227 (–C≡N stretching of cyano group), 1677, 1626 (C=O stretching of carbonyl groups); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.49 (3H, *s*, CH_3), 3.53 (2H, *t*, *J* = 6.4 Hz, C**H**$_2$CH$_2$OH), 3.94 (2H, *t*, *J* = 6.4 Hz, CH$_2$C**H**$_2$OH), 4.80 (1H, *bs*, CH$_2$CH$_2$O**H**), 7.49 (2H, *d*, *J* = 9.0 Hz, Ar-H), 7.68 (2H, *d*, *J* = 9.0 Hz, Ar-H), 14.43 (1H, *s*, NH hydrazone); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 160.7 (Py), 160.3 (Py), 158.7 (Py), 142.2 (Ar), 131.1 (Ar), 129.7 (Ar), 123.7 (Py), 119.9 (Ar), 116.1 (CN), 100.2 (Py), 57.8 (CH$_2$**C**H$_2$OH), 41.5 (**C**H$_2$CH$_2$OH), 16.7 (CH_3); UV–Vis (EtOH) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 430.5 (27700), 264.0 (6540).

*5-((4-Bromophenyl)diazenyl)-6-hydroxy-1-(2-hydroxyethyl)-4-methyl-2-oxo--1,2-dihydropyridine-3-carbonitrile (**9**)*. Yield: 52 %; yellow powder; m.p.: 258.0–258.6 °C; Anal. Calcd. for $C_{15}H_{13}BrN_4O_3$: C, 47.76; H, 3.47; N, 14.85 %.

Found: C, 47.88; H, 3.59; N, 14.98 %; IR (KBr, cm^{-1}): 3491 (N–H stretching of hydrazone unit), 2227 (–C≡N stretching of cyano group), 1679, 1633 (C=O stretching of carbonyl groups); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.50 (3H, *s*, CH_3), 3.55 (2H, *t*, *J* = 6.2 Hz, C**H**$_2$CH$_2$OH), 3.94 (2H, *t*, *J* = 6.2 Hz, CH$_2$C**H**$_2$OH), 4.60 (1H, *bs*, CH$_2$CH$_2$O**H**), 7.55–7.74 (4H, *m*, Ar-H), 14.41 (1H, *s*, NH hydrazone); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 160.7 (Py), 160.3 (Py), 159.3 (Py), 140.8 (Ar), 132.8 (Ar), 123.6 (Py), 119.6 (Ar), 119.4 (Ar), 115.2 (CN), 101.3 (Py), 57.6 (CH$_2$**C**H$_2$OH), 41.6 (**C**H$_2$CH$_2$OH), 16.6 (CH_3); UV–Vis (EtOH) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 435.5 (39840), 275.0 (9240).

*5-((4-Cyanophenyl)diazenyl)-6-hydroxy-1-(2-hydroxyethyl)-4-methyl-2-oxo--1,2-dihydropyridine-3-carbonitrile (**10**)*. Yield: 44 %; yellow powder; m.p.: 279.1–280.9 °C. Anal. Calcd. for $C_{16}H_{13}N_5O_3$: C, 59.44; H, 4.05; N, 21.66 %. Found: C, 59.61; H, 4.16; N, 21.77 %; IR (KBr, cm^{-1}): 3423 (N–H stretching of hydrazone unit), 2230, 2219 (–C≡N stretching of cyano groups), 1683, 1641 (C=O stretching of carbonyl groups); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.51 (3H, *s*, CH_3), 3.56 (2H, *t*, *J* = 6.2 Hz, C**H**$_2$CH$_2$OH), 3.94 (2H, *t*, *J* = 6.2 Hz, CH$_2$C**H**$_2$OH), 4.82 (1H, *bs*, CH$_2$CH$_2$O**H**), 7.83 (2H, *d*, *J* = 9.0 Hz, Ar-H), 7.90 (2H, *d*, *J* = 9.0 Hz, Ar-H), 14.28 (1H, *s*, NH hydrazone); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 160.5 (Py), 160.1 (Py), 159.2 (Py), 145.0 (Ar), 134.1 (Ar), 124.9 (Py), 118.9 (Ar), 118.0 (Ar), 114.9 (CN on heterocyclic), 108.2 (CN substituent), 102.8 (Py), 57.6 (CH$_2$**C**H$_2$OH), 41.8 (**C**H$_2$CH$_2$OH), 16.6 (CH_3); UV–Vis (EtOH) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 42.0 (30120), 268.0 (7080).

*6-Hydroxy-5-((4-methoxyphenyl)diazenyl)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (**11**)*. Yield: 53 %; red powder; m.p. 271.8–272.5 °C. IR (KBr, cm^{-1}): 3433 (N–H stretching of hydrazone unit), 3121 (N–H stretching on heterocyclic ring), 2221 (–C≡N stretching of cyano group), 1655, 1603 (C=O stretching of carbonyl groups); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.50 (3H, *s*, CH_3), 3.80 (3H, *s*, OCH_3), 7.06 (2H, *d*, J = 8.4 Hz, Ar-H), 7.65 (2H, *d*, *J* = 8.4 Hz, Ar-H), 11.96 (1H, *s*, NH heterocyclic), 14.75 (1H, *s*, NH hydrazone); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 161.7 (Py), 161.1 (Py), 160.5 (Py), 158.8 (Ar), 134.7 (Ar), 122.8 (Py), 119.2 (Ar), 115.5 (CN), 115.3 (Ar), 99.5 (Py), 55.7 (OCH_3), 16.6 (CH_3). UV–Vis (EtOH) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 457.0 (13740), 273.5 (3780).

*1-Ethyl-6-hydroxy-5-((4-methoxyphenyl)diazenyl)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (**12**)*. Yield: 73 %; red powder; m.p.: 215.6–217.2 °C; IR (KBr, cm^{-1}): 3433 (N–H stretching of hydrazone unit), 2221 (C≡N stretching of cyano group), 1672, 1627 (C=O stretching of carbonyl groups); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 1.13 (3H, *t*, *J* = 7.0 Hz, C**H**$_3$CH$_2$), 2.50 (3H, *s*, CH_3), 3.80 (3H, *s*, OCH_3), 3.89 (2H, *q*, *J* = 7.0 Hz, CH$_3$C**H**$_2$), 7.06 (2H, *d*, *J* = 9.0 Hz, Ar-H), 7.71 (2H, *d*, *J* = 9.0 Hz, Ar-H), 14.81 (1H, *s*, NH hydrazone); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 161.8 (Py), 161.2 (Py), 160.6 (Py), 158.9 (Ar),

134.8 (Ar), 122.9 (Py), 119.5 (Ar), 115.4 (Ar), 115.3 (CN), 99.6 (Py), 55.8 (OCH_3), 34.5 (**C**H_3CH_2), 16.6 (CH_3), 12.9 (**C**H_3CH_2); UV–Vis (EtOH) (λ_{max} / / nm (ε / L mol^{-1} cm^{-1})): 460.0 (15380), 273.5 (4180).