Supplemetary material

Experimental and theoretical study on solvent and substituent effect in 3-(4-substitutedanilino)isobenzofuran-1(3*H*)-ones

NEVENA Ž. PRLAINOVIĆ[1], MILICA P. RANČIĆ[2], IVANA STOJILJKOVIĆ[2], JASMINA B. NIKOLIĆ[3*], SAŠA Ž. DRMANIĆ[3], ISMAIL AJAJ[4], and ALEKSANDAR D. MARINKOVIĆ[3]

[1]*Innovation Center, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia*

[2]*Faculty of Forestry, University of Belgrade, KnezaVišeslava 1, 11030 Belgrade, Serbia*

[3]*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia*

[4] *Faculty of Arts And Science, The university of El-margeb, Mesallata, Libya*

[*]corresponding author, e-mail: jasmina@tmf.bg.ac.rs

Table SI. Solvent parameters used in Kamlet–Taft equation[1,2]

Solvent	π	β	α
1,2-Dichloroethane	0.81	0.1	0
1-Decanol	0.45	0.82	0.7
Dichloromethane	0.82	0.1	0.13
Dioxolane	0.69	0.45	0
Ethane-1,2-diol	0.9	0.52	0.9
Ethanol	0.54	0.75	0.86
Water	1.09	0.47	1.17
Hexane	0	0	-0.04
2-Methyl-1-propanol	0.4	0.84	0.79
2-Propanol	0.48	0.84	0.76
Methanol	0.6	0.66	0.98
1-Butanol	0.47	0.84	0.84
1-Propanol	0.52	0.9	0.84
2-Butanol	0.4	0.8	0.69
2-Methyl-2-propanol	0.41	0.93	0.41
Tetrahydofuran	0.58	0.55	0

Table SII. Solvent parameters used in Catalán equation[3]

Solvent	SP	SdP	SA	SB
1,2-Dichloroethane	0.77	0.74	0.03	0.13
1-Decanol	0.72	0.38	0.26	0.91
Dichloromethane	0.76	0.77	0.04	0.18
Dioxolane	0.78	0.91	0.72	0.53
Ethane-1,2-diol	0.63	0.78	0.4	0.66
Ethanol	0.68	0.99	1.06	0.03
Water	0.62	0	0	0.06
Hexane	0.66	0.68	0.31	0.83
2-Methyl-1-propanol	0.63	0.8	0.28	0.83
2-Propanol	0.6	0.9	0.6	0.54
Methanol	0.67	0.65	0.34	0.8
1-Butanol	0.65	0.75	0.37	0.78
1-Propanol	0.66	0.7	0.22	0.89
2-Butanol	0.63	0.73	0.16	0.93
2-Methyl-2-propanol	0.71	0.63	0	0.59

Experimental

Materials

All chemicals used in this study were reagent grade or p.a. quality, and used as received. Phthalaldexyde acid, aniline, glacial acetic acid, benzaldehyde, 4-methylbenzaldehyde, 4-methoxybenzaldehyde, 4-hydroxybenzaldehyde, 4-fluorobenzaldehyde, 4-chlorobenzaldehyde, 4-nitrobenzaldehyde, 4-acetylbenzaldehyde, 2-aminopyridine and 3-aminopyridine were purchased from Sigma Aldrich. All used solvents were of spectroscopic quality (Table SI).

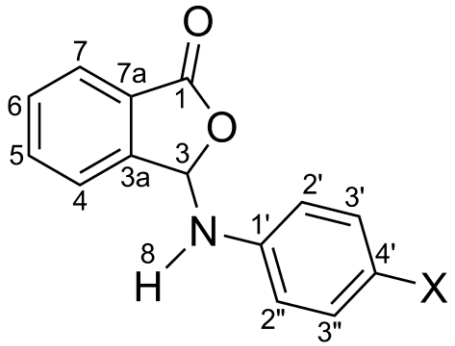

Fig. S1. Phthalide structure

Results of the characterization

3-(phenylamino)isobenzofuran-1(3H)-one (1). Colorless needles, 0.55 g (74 %) yield, mp 179-180°C, IR (ATR): 3334(N-H), 3038 (C-H, Ar), 1734 (C=O), 1605 (N-H), 1285 (C-N), 1206 (C-O-C), 1098 (C-O-C) cm^{-1}; 1H NMR (DMSO-d_6): δ 6.54 (d, 1H, H8, 6.79 (t, H2'), 6.97 (t, H4'), 7.13 (d, H3), 7.20-7.28 (m, 2H, H3'), 7.70-7.76 (m, 2H, H4, H6), 7.84-7.92 (m, 2H, H5, H7). ^{13}C NMR (500 MHz DMSO-d_6, δ): 88.53, 114.39, 114.84, 119.84, 124.62, 125.43, 129.64, 131.04, 134.91, 145.67, 146.38, 169.70.

Elemental analysis for $C_{14}H_{11}NO_2$: Calculated. C 74.65, H 4.92, N 6.22, O 14.21; found C 74.69, H 4.91, N 6.17, O 14.23.

3-((4-methylphenyl)amino)isobenzofuran-1(3H)-one (2). Colorless needles, 0.58 g (78 %) yield, mp 183-185ºC, IR (ATR): 3345 (N-H), 3020 (C-H, Ar), 1736 (C=O), 1615 (N-H), 1285 (C-N), 1218 (C-O-C), 1097 (C-O-C) cm^{-1}; 1H NMR (DMSO-d_6): δ2.23 (s, 3H, CH_3), 6.46 (d, 1H, H8), 6.87 (dd, 2H, H2'), 7.05 (dd, 2H, H3'), 7.13 (d, 1H, H3), 7.66-7.75 (m, 2H, H4, H6), 7.81-7.91 (m, 2H, H5, H7). ^{13}C NMR (500 MHz DMSO-d_6, δ): 169.39, 159.48, 146.15, 142.96, 134.51, 130.68, 129.78, 129.71, 128.15, 127.79, 124.87, 124.31, 114.70, 88.75, 20.33.

Elemental analysis for $C_{15}H_{13}NO_2$: Calculated. C 75.30, H 5.48, N 5.85, O 13.37; found C 75.31, H 5.48, N 5.80, O 13.41.

3-((4-methoxyphenyl)amino)isobenzofuran-1(3H)-one (3). Colorless needles, 0.64 g (83 %) yield, mp 143-144°C, IR (ATR): 3321 (N-H), 3031 (C-H, Ar), 1740(C=O), 1597 (N-H), 1255 (C-N), 1113 (C-O-C), 1076 (C-O-C) cm^{-1}; 1H NMR (DMSO-d_6): δ 2.23 (s, 3H, CH_3), 6.52 (d, 1H, H8), 6.88 (dd, 2H, H2'), 7.05 (dd, 2H, H3'), 7.13 (d, 1H, H3), 7.66-7.73 (m, 2H, H4, H6), 7.85-7.91 (m, 2H, H5, H7). ^{13}C NMR (500 MHz DMSO-d_6, δ): 169.34, 159.80, 153.33, 146.03, 139.19, 139.04, 134.34, 130.66, 128.05, 124.95, 124.50, 116.14, 115.06, 114.76, 89.50.

Elemental analysis for $C_{15}H_{13}NO_3$: Calculated. C 70.58, H 5.13, N 5.49, O 18.80; found C 70.51, H 5.17, N 5.51, O 18.81.

3-((4-hydroxyphenyl)amino)isobenzofuran-1(3H)-one (4). Colorless needles, 0.65 g (87 %) yield, mp 180-183°C, IR (ATR): 3352 (N-H), 3177 (C-H, Ar), 1710 (C=O), 1616 (N-H), 1258 (C-N), 1208 (C-O-C), 1108 (C-O-C) cm^{-1}; 1H NMR (DMSO-d_6):): δ 6.48 (d, 1H, H8), 6.69 (dd, 2H, H2'), 6.87 (dd, 2H, H3'), 7.63 (d, 1H, H3), 7.66-7.71 (m, 2H, H4, H6), 7.78-7.90 (m, 2H, H5, H7). (500 MHz DMSO-d_6, δ): 169.30, 159.09, 151.75, 145.34, 138.13, 134.10, 130.59, 128.48, 125.66, 125.24, 124.80, 117.04, 116.21, 89.74.

Elemental analysis for $C_{14}H_{11}NO_3$: Calculated. C 69.70, H 4.60, N 5.81, O 19.90; found C 69.80, H 4.57, N 5.79, O 19.84.

3-((4-fluorophenyl)amino)isobenzofuran-1(3H)-one (5). Colorless needles, 0.59 g (79 %) yield, mp 188-189°C, IR (ATR): 3330 (N-H), 3044 (C-H, Ar), 1728 (C=O), 1610 (N-H), 1229 (C-N), 1208 (C-O-C), 1108 (C-O-C) cm^{-1}; 1H NMR (DMSO-d_6):): δ 6.52 (d, 1H, H8), 6.896 (dd, 2H, H2'), 7.07 (dd, 2H, H3'), 7.15 (d, 1H, H3), 7.67-7.76 (m, 2H, H4, H6), 7.86-7.92 (m, 2H, H5, H7). (500 MHz DMSO-d_6, δ): 169.32, 158.81, 154.14, 145.98, 141.92, 134.60, 130.77, 127.67, 124.92, 124.30, 116.00, 115.80, 115.64, 88.62.

Elemental analysis for $C_{14}H_{10}FNO_2$: Calculated. C 69.13, H 4.14, F 7.81, N 5.76, O 13.16; found C 69.01, H 4.20, F 7.76, N 5.86, O 13.17.

3-((4-chlorophenyl)amino)isobenzofuran-1(3H)-one (6). Colorless needles, 0.54 g (72 %) yield, mp 180-182°C, IR (ATR): 3341 (N-H), 3020 (C-H, Ar), 1732 (C=O), 1560 (N-H), 1303 (C-N), 1206 (C-O-C), 1090 (C-O-C) cm^{-1}; 1H NMR (DMSO-d_6):): δ 6.52 (d, 1H, H8), 6.88 (dd, 2H, H2'), 7.14 (d, 1H, H3), 7.128 (dd, 2H, H3'), 7.71-7.76 (m, 2H, H4, H6), 7.82-7.92 (m, 2H, H5, H7). ^{13}C NMR (500 MHz DMSO-d_6, δ): 169.26, 159.45, 145.86, 144.47, 134.68, 130.83, 129.10, 127.55, 124.96, 124.32, 123.08, 116.09, 116.03, 87.72.

Elemental analysis for $C_{14}H_{10}ClNO_2$: Calculated. C 64.75, H 3.88, Cl 13.65, N 5.39, O 12.32; found C 64.61, H 3.74, Cl 13.69, N 5.43, O 12.53.

3-((4-acetylphenyl)amino)isobenzofuran-1(3H)-one (7). Colorless needles, 0.50 g (66 %) yield, mp 246-247°C, IR (ATR): 3340 (N-H), 3020 (C-H, Ar), 1760 (C=O), 1596 (N-H), 1284 (C-N), 1220 (C-O-C), 1107 (C-O-C) cm^{-1}; 1H NMR (DMSO-d_6): δ 2.50 (s, 3H, CH_3), 6.55 (d, 1H, H8), 7.05 (dd, 2H, H2'), 7.25 (d, 1H, H3), 7.71 (dd, 2H, H4, H6), 7.73-7.79 (m, 2H, H3'), 7.85-7.95 (m, 2H, H5, H7). ^{13}C NMR (500 MHz DMSO-d_6, δ): 196.18, 169.18, 159.16, 150.02, 145.70, 134.81, 130.92, 130.49, 128.62, 127.35, 125.04, 124.37, 113.67, 113.56, 86.53, 26.49.

Elemental analysis for $C_{16}H_{13}NO_3$: Calculated. C 71.90, H 4.90, N 5.24, O 17.96; found C 71.93, H 4.86, N 5.28, O 17.93.

3-((4-nitrophenyl)amino)isobenzofuran-1(3H)-one (8). Colorless needles, 0.48 g (64 %) yield, mp 241-243°C, IR (ATR): 3330 (N-H), 3044 (C-H, Ar), 1728 (C=O), 1610 (N-H), 1229 (C-N), 1208 (C-O-C), 1083 (C-O-C) cm^{-1}; 1H NMR (DMSO-d_6): δ 6.58 (d, 1H, H8), 7.10 (dd, 2H, H2'), 7.26 (d, 1H, H3), 7.71-7.82 (m, 2H, H4, H6), 7.86-7.96 (m, 2H, H5, H7),8.17 (dd, 2H, H3'). ^{13}C NMR (500 MHz DMSO-d_6, δ): 168.99, 159.69, 152.04, 145.35, 139.47, 134.94, 131.09, 127.12, 126.11, 125.14, 124.43, 113.83, 113.72, 85.70.

Elemental analysis for $C_{14}H_{10}N_2O_4$: Calculated. C 62.22, H 3.73, N 10.37, O 23.68; found C 62.18, H 3.69, N 10.40, O 23.73.

3-(2-pyridynylamino)isobenzofuran-1(3H)-one (9). Colorless needles, 0.43 g (57 %) yield, mp 206-207°C, IR (ATR): 3329 (N-H), 3040 (C-H, Ar), 1751 (C=O), 1594 (N-H), 1262 (C-N), 1225 (C-O-C), 1063 (C-O-C) cm^{-1}; 1H NMR (DMSO-d_6): δ 6.92 (s, 1H, CH), 7.25 (m, 1H, H4'), 7.46 (m, 1H, H2'), 7.67-7.71 (m, 2H, H4, H6), 7.85-7.89 (m, 1H, H3''), 7.97-8.03 (m, 2H, H5, H7), 8.48 (m, 1H, H3'). ^{13}C NMR (500 MHz DMSO-d_6, δ): 169.34, 161.31, 159.95, 158.60, 146.31, 134.58, 130.46, 127.46, 124.77, 124.05, 113.72, 113.60, 84.58.

Elemental analysis for $C_{13}H_{10}N_2O_2$: Calculated. C 69.02, H 4.46, N 12.38, O 14.14; found C 69.00, H 4.39, N 12.44, O 14.17.

3-(3-pyridynylamino)isobenzofuran-1(3H)-one (10). Colorless needles, 0.44 g (59 %) yield, mp 159-160°C, IR (ATR): 3329 (N-H), 3042 (C-H, Ar), 1741 (C=O), 1583 (N-H), 1285 (C-N), 1215 (C-O-C), 1094 (C-O-C) cm^{-1}; 1H NMR (DMSO-d_6): δ 6.64 (d, 1H, CH), 7.46 (d, 2H, H5, H7), 7.18-7.29 (m, 2H, H4, H6), 7.72-7.90 (m, 2H, H2''), 8.06 (dd, 1H, H2'), 8.28 (dd, 1H, H4'). ^{13}C NMR (500 MHz DMSO-d_6, δ): 169.21, 159.94, 145.81, 141.73, 140.81, 137.28, 134.75, 130.90, 127.47, 125.01, 124.34, 120.78, 87.30.

Elemental analysis for $C_{13}H_{10}N_2O_2$: Calculated. C 69.02, H 4.46, N 12.38, O 14.14; found C 68.94, H 4.45, N 12.35, O 14.26.

Table SIII. Results of enerigies of optimized molecules by DFT/B3LYP 6-31G(d,p) method

Compound	Energy (Hartree)
1	-745.3479
2	-784.6680
3	-859.8708
4	-820.5657
5	-844.5781
6	-1204.9419
7	-898.0002
8	-949.8508
9	-761.3929
10	-761.3810

References

1. M.J. Kamlet, J.L.M. Abboud, M.H. Abraham, R. W.Taft,. *J. Org. Chem.***48** (1983) 2877
2. Y.Marcus, *Chem. Soc. Rev.***22** (1993) 409
3. J.Catalán,. *J. Phys. Chem. B***113** (2009) 5951