Photoinduced intramolecular charge transfer to meta-position of benzene ring in 6-aminophthalides.

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SUPPLEMENTARY INFORMATION

Description of synthetic procedures

6-Dimethylamino-3H-isobenzofuran-1-one (**6-DMAPd**, referred to in this work as 6-dimethylaminophthalide) was prepared quantitatively from 6-nitro-3H-isobenzofuran-1-one by simultaneous hydrogenation and reductive methylation over 10% Pd/C catalyst in the presence of 35% aqueous formaldehyde while maintaining conditions similar to those reported by Stanetty *et al.*[1], except the reaction was carried out under normal pressure of hydrogen. White crystals from n-hexane, m. p.: 122° C, (lit. 121-122° C)[1].

6-Methylamino-3H-isobenzofuran-1-one (**6-MAPd**, referred to in this work as 6-methylaminophthalide) was isolated by column chromatography over neutral alumina (III grade activity) with 1:1 hexane-methylene chloride from the reaction product obtained as above when the reaction was terminated after 4/5 of the molar equivalent of hydrogen had been consumed. Yield approx. 5%, pale yellow crystals from n-hexane-methylene chloride, m. p.: 99° C. ^{1}H NMR, δ(ppm): 2.89(3H, s), 3.80(1H, bs), 5.22(2H, s), 6.95(1H, dd; J=8.30 and 2.19 Hz), 7.03(1H, d; J=2.19 Hz), 7.24(1H, d; J=8.30 Hz); ^{13}C NMR, δ(ppm): 30.77(q), 69.66(t), 105.86(d), 120.35(d), 122.40(d), 126.88(s), 135.24(s), 150.15(s), 171.97(s).

6-Nitro-3H-isobenzofuran-1-one under the same hydrogenation conditions as above (but without formaldehyde) gave also quantitatively **6-amino-3H-benzofuran-1-one** (**6-APd**, referred to in this work as 6-aminophthalide). White crystals from ethanol or methylene chloride, m. p.: 183-184° C (lit.: 179-181° C [2]; 182° C [3]).

6-Aminophthalide (6-APd) subjected to the modified Skraup reaction conditions[4] afforded 3H-furo[3,4-f]quinoline-1-one (with 28% yield). White crystals from n-hexane-methylene chloride, m. p.: 199-200° C. ^{1}H NMR, δ(ppm): 5.54(2H, s), 7.62(1H, dd; J=8.30 and 4.27 Hz), 7.78(1H, d; J=8.67 Hz), 8.38(1H, d; J=8.67 Hz), 9.05(1H, m), 9.25(1H, dm; J=8.30 Hz); ^{13}C NMR, δ(ppm): 68.39(t), 120.46(s) (?), 122.20(d), 123.51(d), 131.47(d), 136.78(d), 148.23(s), 2*148.51 (s and s) (?), 151.62(d), 170.60(s). From the quinoline derivative after hydrogenation over Pt in glacial acetic acid under normal pressure **6,7,8,9-tetrahydro-3H-furo[3,4-f]quinoline-1-one** (**6-MAPd-C**) was obtained with 95% yield. Pale yellow crystals from n-hexane-methylene chloride, m. p.: 145-146° C. ^{1}H NMR, δ(ppm): 1.95(2H, m),

3.20(2H, t; J=6.47 Hz), 3.34(2H, t; J=5.49 Hz), 3.70(1H, bs), 5.13(2H, s), 6.74(1H, d; J=8.06 Hz), 7.00(1H, d; J=8.06 Hz); ^{13}C NMR, δ(ppm): 21.04(t), 22.16(t), 41.59(t), 68.83(t), 119.57(d), 120.47(d), 120.87(s), 123.27(s), 135.56(s), 145.50(s), 171.91(s).

Subsequent reductive methylation of the latter compound under conditions cited before yielded quantitatively **6-methyl-6,7,8,9-tetrahydro-3H-furo[3,4-f]quinoline-1-one** (**6-DMAPd-C**). White crystals from n-hexane, m. p.: 86-87° C. ^{1}H NMR, δ(ppm): 2.00(2H, m), 2.93(3H, s), 3.26(4H, m), 5.14(2H, s), 6.86(1H, d; J=8.30 Hz), 7.10(1H, d; J=8.30 Hz); ^{13}C NMR, δ(ppm): 21.36(t), 22.54(t), 39.92(q), 51.01(t), 68.59(t), 116.88(d), 119.68(d), 122.65(s), 122.94(s), 134.16(s), 147.38(s), 172.02(s).

All melting points are uncorrected. Identity of the newly obtained compounds was confirmed by their satisfactory elemental analyses, absorption, emission and ^{1}H and ^{13}C NMR spectra. ^{1}H and ^{13}C NMR spectra were recorded with Varian Unity plus-200 spectrometer in deuteriochloroform with TMS as internal standard at 200 and 50 MHz, respectively.

Fluorescence excitation spectrum of 6-DMAPd in acetonitrile vs. absorption spectrum

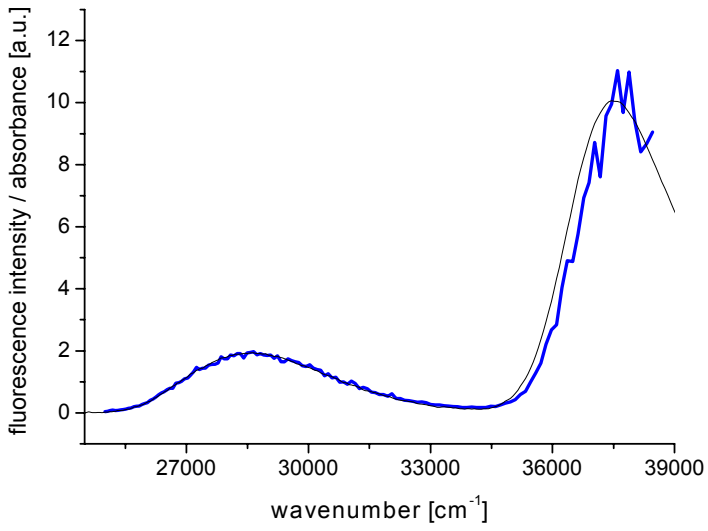

Figure A: Fluorescence excitation spectrum of 6-DMAPd in acetonitrile (thick line) compared with the absorption spectrum (thin line). Both spectra are normalised to the maximum of the first absorption band (at 28550 cm^{-1}).

Molecular orbitals involved in the lowest absorption band in 6-APd

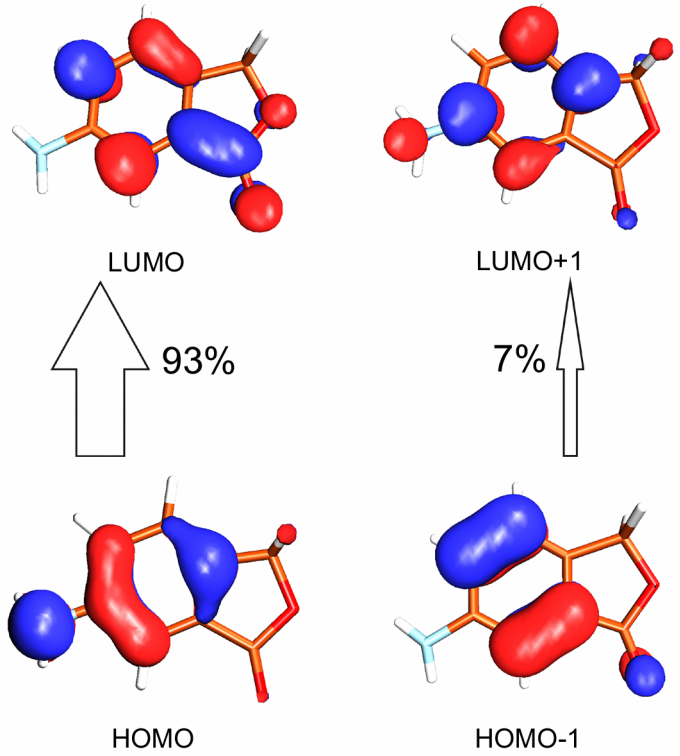

Figure B: Molecular orbitals involved in the transitions making up the lowest absorption band in 6-aminophthalide (6-APd). The dominating transition (contribution of 97%) on the left side involves promotion of electron from HOMO to LUMO orbital and the weaker transition (contribution of 3%) – from HOMO-1 to LUMO+1 orbital.

Magnetic circular dichroism (MCD) spectra of 6-DMAPd in acetonitrile

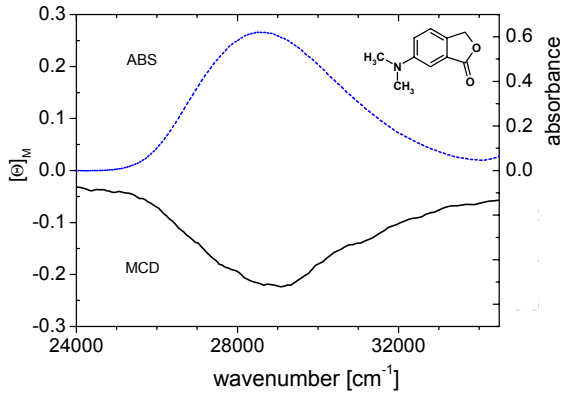

Figure C: Room temperature absorption (dashed line) and MCD spectra for 6-DMAPd in acetonitrile.

Dependence of ln(k_{nr}) on S_1 transition energy

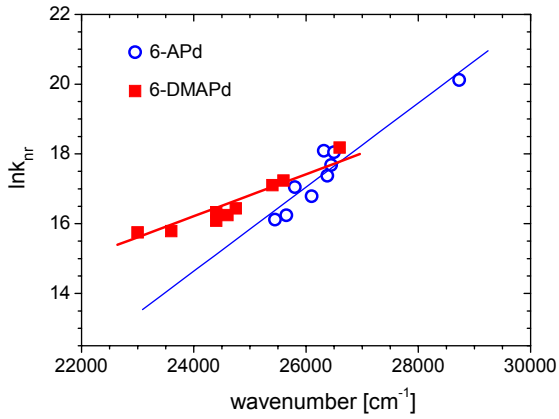

Figure D: Dependence of ln(k_{nr}) on S_1 transition energy.

References

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