Supporting Information

for

Geometrical Effects on Intramolecular Quenching of Aromatic Ketone (p,p*) Triplets by Remote Phenolic Hydrogen Abstraction

by

Edward C. Lathioor, William J. Leigh*, and Michael J. St. Pierre

Experimental details. Synthetic procedures and spectroscopic/analytical data for all compounds.

Figure 1. Triplet-triplet absorption spectra of compounds **5a,b** in deoxygenated acetonitrile solution at 23.0 ± 0.2 ^{o}C.

Figure 2. Triplet-triplet absorption spectra of compounds **6a,b** in deoxygenated acetonitrile solution at 23.0 ± 0.2 ^{o}C.

1. Experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC200 (200 MHz) or AC300 (300 MHz) spectrometers in deuterated solvents, and are reported in parts per million downfield from tetramethylsilane. Ultraviolet absorption spectra were recorded on a Hewlett-Packard HP8451 UV spectrometer or a Cary 300 spectrometer. Mass spectra and exact masses were recorded on a VG Analytical ZABE mass spectrometer employing a mass of 12.000000 for carbon. Infrared spectra were recorded on a Biorad FTS-40 FTIR spectrometer and are reported in wavenumbers. Melting points were determined on a polarizing microscope fitted with a Mettler hot stage controlled by a Mettler FP80 processor, and are not corrected. Gas chromatographic analyses employed a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3396A recording integrator, and a 15-m x 0.53-mm DB-17A column from Chromatographic Specialties. Radial chromatography was carried out using a Chromatotron® (Harrison Research) equipped with 4-mm silica gel 60 with gypsum (EM Science) thick-layer plates. Flash column chromatography was performed with silica gel 60 from Silicycle, Inc. (100-400 mesh). Elemental analyses were performed by Guelph Chemical Laboratories, Ltd.

Acetone (Caledon Reagent) was stored over and distilled from anhydrous potassium carbonate, acetonitrile (Caledon Reagent) was dried by first distilling from calcium hydride and then either standing over activated 4 Å molecular sieves or repeated passage through a bed of activated Brockmann neutral alumina (Aldrich). Benzene (BDH or Caledon, thiophene-free) was purified by washing three times with concentrated sulfuric acid, followed by repeated washings with saturated aqueous sodium bicarbonate, water and brine, and then finally distilled from sodium. Hexane (Caledon Reagent) was distilled before use. Pyridine (Fisher Reagent) was

stored over and distilled from barium oxide. All other solvents were spectroscopic or HPLC grade and used as received from the suppliers (Caledon or Fisher).

3-Hydroxyacetophenone, 4-hydroxyacetophenone, 3-methoxyacetophenone, and 4-methoxyacetophenone (Aldrich) were either recrystallized from water/ethanol mixtures or used as received. 1,3-Cyclohexadiene (Aldrich) was bulb-to-bulb distilled and stored over nitrogen at -20°C. 1-Methylnaphthalene (Aldrich) and *p*-cresol (Caledon) were vacuum-distilled. *p*-Toluenesulfonyl chloride(Aldrich) was purified according to the method of Fieser and Fieser[1] and stored under nitrogen. 1-Bromo-2-(4-methoxyphenyl)ethane was prepared by brominating 4-methoxyphenethyl alcohol (Aldrich) with PBr_3 in dry benzene according to the method of Bachmann and Thomas.[2] All other reagents were used as received from Caledon or Aldrich Chemical Co. All reactions save for the tosylate ester hydrolyses were performed under nitrogen.

The tosylate esters were prepared according to the general method of Fieser and Fieser,[1] for which the preparation of **1-tosyloxy-2-(3-tosyloxyphenyl)ethane** is typical. In an oven-dried 250-mL ground-joint Erlenmeyer flask suspended in an ice/salt bath at -3.5 °C was placed 2-(3-hydroxyphenyl)ethanol (2.64 g, 0.019 mol), freshly distilled pyridine (70 mL) and an oven-dried stirbar. After stirring for 10 minutes, *p*-toluenesulfonyl chloride (15.2 g, 0.08 mol) was added all at once. The clear yellow solution was stoppered and stirred for 90 minutes at 0-2 °C, during which time a fine white precipitate of pyridinium hydrochloride was formed. The mixture was then stored at -15 °C for 12 hours and at 9°C for 36 hours. The orange reaction mixture was poured into ice water (400 mL) and then extracted with ether (2 x 200 mL, 1 x 50 mL). The combined organic fractions were washed with ice cold 50% HCl (2 x 200 mL) and then water (2 x 200 mL), dried over anhydrous magnesium sulfate and filtered through a coarse frit. The pale yellow solution was stripped of solvent on the rotary evaporator to yield a solid residue, which

was recrystallized from 10:3:2 ligroin (30-60):ether:dichloromethane to give colorless plates of the desired product (4.05 g, 0.0095 mol, 48%). m.p. 81-84°C; ^{1}H NMR ($CDCl_3$) δ = 2.42 (s, 3H), 2.43 (s, 3H), 2.85 (t, J = 6.8 Hz, 2H), 4.11 (t, J = 6.8 Hz, 2H), 6.71 (m, 1H), 6.83 (m, 1H), 6.98 (d, J = 7.7 Hz, 1H), 7.14 (t, J: 7.9 Hz, 2H), 7.25-7.31 (m, 2H), 7.62-7.69 (m, 2H); ^{13}C NMR ($CDCl_3$), δ = 21.6 (2 carbons), 34.9, 69.8, 120.8, 122.8, 127.7, 127.8, 128.5, 129.7, 129.8 (2 carbons), 132.3, 132.7, 138.4, 144.9, 145.5, 149.7; IR ($CDCl_3$; cm^{-1}) 3157 (w), 2985 (w), 2256 (m), 1795 (w), 1653 (w), 1600 (w), 1487 (w), 1375 (m), 1191 (m), 1179 (m), 1133 (w), 1095 (w), 909 (s), 734 (s); MS, m/e (I): 274 (25), 155 (68), 119 (26), 91 (100), 65 (73), 52 (14), 41 (14); HRMS: Calcd. for $C_{22}H_{22}O_6S_2$: 446.08586. Found: 446.085776.

1-Tosyloxy-2-(3-methoxyphenyl)ethane. This material was obtained in ~82% yield as a yellow oil, and contained ~5% 1-chloro-2-(3-methoxyphenyl)ethane as an impurity. The IR and ^{1}H NMR spectra were similar to those reported in the literature for this compound.[3,4] ^{13}C NMR: ($CDCl_3$) δ 21.6, 35.4, 55.1, 70.6, 112.4, 114.5, 121.3, 127.8, 129.6, 129.9, 132.9, 137.8, 144.8, 159.8.

1-Tosyloxy-2-(4-tosyloxyphenyl)ethane. Using the genreal procedure outlined above for the tosylate preparation, the major product here was 1-chloro-2-(4-tosyloxyphenyl)ethane. The reaction was not optimized, but the amount of this impurity could be reduced with shorter reaction times and always keeping the reaction below 5 °C. Yield, 16%; m.p. 75.7-76.8°C; ^{1}H NMR: ($CDCl_3$) δ 2.42 (s, 3H), 2.43 (s, 3H), 2.89 (t, J = 6.8 Hz, 2H), 4.14 (t, J = 6.8 Hz, 2H), 6.83 (d, J = 6.6 Hz, 1H), 7.00 (d, J = 8.7 Hz, 2H), 7.25-7.31 (m, 4H), 7.65 (t, J = 8.0 Hz, 4H); ^{13}C NMR: ($CDCl_3$) δ 21.6, 21.7, 34.6, 70.0, 122.4, 127.7, 128.4, 129.8 (2 carbons), 130.0, 132.3, 132.7, 135.4, 144.9, 145.4, 148.5; IR (KBr; cm^{-1}): 3094 (w), 3056 (w), 2954 (w), 1718 (m), 1605 (m), 1497 (m), 1374 (s), 1202 (m), 1178 (s), 1089 (m), 967 (m), 899 (m), 866 (m), 844 (m), 814

(m), 766 (m), 709 (m), 664 (m), 558 (m); MS, m/e (I): 274 (16), 155 (38), 120 (17), 91 (100), 65 (26).

Synthesis of 5-7.

4-[2-(3-hydroxyphenyl)ethoxy]acetophenone (**5a**). In an oven-dried 100-mL round bottom flask equipped with a magnetic stirring bar and reflux condenser were placed 1-tosyl-2-(3-tosyloxyphenyl)ethane (1.0 g, 2.24 mmol), anhydrous potassium carbonate (0.42 g, 3.04 mmol), 4-hydroxyacetophenone (0.29 g, 2.13 mmol) and dry acetone (30 mL). The mixture was refluxed for one week, filtered, and the solvent was removed on the rotary evaporator. The resulting light brown oil was diluted with aqueous HCl (3 M, 10 mL) until acidic and taken up into ether (2 x 20 mLs) and ethyl acetate (20 mL). After separation, the orange organic fraction was washed with brine (30 mL), aqueous HCl (1 M, 30 mL) and brine again (25 mL), dried over anhydrous $MgSO_4$, filtered, and the solvent removed on the rotary evaporator. ^{1}H NMR analysis indicated that the crude mixture consisted largely of the tosylate ester of **5a**, contaminated with a small amount of unreacted 4-hydroxyacetophenone. This mixture was hydrolysed by refluxing in methanol (20 mL) containing anhydrous potassium carbonate (2.6 g, 20 mmol) for 6 days. Work-up in similar fashion to that described above yielded crude **5a** as a dark oil (0.53 g). The compound was purified by radial chromatography using 20% ethyl acetate in hexanes as eluant, and recrystallized twice from methanol to give **5a** as a white powder (0.1 g, 0.4 mmol, 20%). mp. 117.4 - 118.5°C; ^{1}H NMR: ($CDCl_3$) δ 2.53 (s, 3H), 3.05 (t, J = 7.0 Hz, 2H), 4.20 (t, J = 7.0 Hz, 2H), 5.20 (br s, 1H), 6.70-6.84 (m, 3H), 6.89 (d, J = 9 Hz, 2H), 7.17 (t, J = 7.8 Hz, 1H), 7.90 (d, J = 9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 26.3, 35.4, 68.7, 113.6, 114.2, 115.9, 121.3, 129.7, 130.1, 130.2, 130.6, 139.6, 155.8, 162.8, 197.1; UV λ_{max} (MeCN) 266 nm (ε 15000 $M^{-1}cm^{-1}$), sh. 198,

214 nm; IR (KBr; cm^{-1}) 3334 (br s), 3262 (w), 2953 (w), 2926 (w), 1653 (s), 1598 (s), 1583 (s), 1512 (m), 1486 (w), 1424 (w), 1362 (m), 1312 (w), 1271 (s), 1158 (m), 1119 (w), 1070 (w), 1017 (m), 960 (w), 885 (w), 834 (s), 787 (m), 705 (m), 586 (m); MS, m/e (I): 256 (20), 236 (8), 165 (25), 121 (100), 107 (10), 97 (15), 83 (23), 69 (40), 55 (38); HRMS: Calcd. for $C_{16}H_{16}O_3$: 256.1099. Found: 256.1119; Anal: Calcd $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.84; H, 6.42.

3-[2-(4-hydroxyphenyl)ethoxy]acetophenone (**6a**). In an oven-dried 100-mL round bottom flask equipped with a magnetic stirring bar and reflux condenser were placed 1-tosyl-2-(4-tosyloxyphenyl)ethane (1.63 g, 3.7 mmol), anhydrous potassium carbonate (0.76 g, 5.5 mmol), 3-hydroxyacetophenone (0.45 g, 3.3 mmol) and dry acetone (20 mL). The mixture was refluxed for 48 hours, filtered, and the solvent was removed on the rotary evaporator. The resulting light brown oil was dissolved in ether (20 mL) and shaken with aqueous HCl (3 M, 10 mL). After separation, the bright yellow ether layer was washed with water (2x20mL) and the original aqueous layer was extracted with ether (2x15mL). The combined ether extracts were dried over anhydrous $MgSO_4$, filtered, and the solvent removed on the rotary evaporator. ^{1}H NMR analysis indicated that the crude mixture consisted largely of the tosylate ester of **6a**, contaminated with a small amount of 4-tosyloxystyrene and unreacted 3-hydroxyacetophenone. This mixture was hydrolysed by refluxing in methanol (20 mL) containing anhydrous potassium carbonate (3.8 g, 27 mmol) for 72 hours. Work-up in similar fashion to that described above yielded crude **6a** as an oily solid (0.9 g). The compound was purified by radial chromatography using chloroform as eluant, and recrystallized from 30% ethyl acetate in hexanes to give colorless needles of **6a** (0.85 g, 0.33 mmol, 10%): mp. 71.9 - 72.6°C; ^{1}H NMR ($CDCl_3$) δ 2.57 (s, 3H), 3.02 (t , J = 7.0 Hz, 2H), 4.16 (t, J = 7.0 Hz, 2H), 4.76 (s, 1H), 6.76 (d, J = 8.4 Hz, 2H), 7.06 - 7.10 (m, 1H), 7.14 (d,

J = 8.4 Hz , 2H), 7.33 (t, J = 7.9 Hz, 1H), 7.45 (m, 1H), 7.52 (d, J = 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.7, 34.8, 69.1, 113.1, 115.4, 120.1, 121.1, 129.6, 130.2 (2 carbons), 130.3, 138.4, 154.2, 159.1, 198.1; UV λ_{max} (MeCN) 216 nm (ε 17800 $M^{-1}cm^{-1}$), sh 196, 244, 280, 302 nm; IR (KBr; cm^{-1}) 3244 (br s), 2942 (w), 2855 (w), 1667 (s), 1614 (m), 1580 (m), 1517 (s), 1449 (s), 1358 (m), 1298 (s), 1269 (s), 1221 (s), 1108 (m), 1044 (s), 974 (m), 885 (m), 833 (m), 774 (s), 684 (s), 590 (m), 555 (w); MS, m/e (I) 256 (15), 165 (5), 121 (100), 107 (30), 103 (8), 91 (10), 77 (15); HRMS: Calcd. for $C_{16}H_{16}O_3$: 256.1099. Found: 256.1116; Anal: Calcd $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.85; H, 6.22.

3-[2-(3-hydroxyphenyl)ethoxy]acetophenone (**7a**). This compound was prepared in a similar fashion to **6a**, except that 3-hydroxyacetophenone (0.22 g, 1.6 mmol) was coupled to 1-tosyl-2-(3-tosyloxyphenyl)ethane (0.805 g, 1.80 mmol) in the presence of anhydrous potassium carbonate (0.26 g, 1.9 mmol) in refluxing acetone (10 mL) over 48 hours. After workup in similar fashion to that of **6a**, the crude tosylate ester was hydrolysed by refluxing with anhydrous potassium carbonate (5.0 g, 36 mmol) in methanol (13 mL) for four days. Final workup yielded a mixture of **7a** and 3-hydroxystyrene, which were separated by column chromatography utilizing 30% ethyl acetate in hexanes as eluant to yield the desired material as a colorless solid. Recrystallization from methanol yielded **7a** as colorless plates (0.15 g, 0.6 mmol, 36%): mp. 88.7 - 90.6°C; ^{1}H NMR ($CDCl_3$) δ 2.57 (s, 3H), 3.04 (t, J = 7.0 Hz, 2H), 4.19 (t, J = 7.0 Hz, 2H), 5.25 (br s, 1H), 6.72 (m, 1H), 6.77 (s, 1H), 6.83 (d, J = 7.5 Hz, 1H), 7.08 (m, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.33 (t, J = 7.9 Hz, 1H), 7.46 (m, 1H), 7.50 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.7, 35.5, 68.7, 113.2, 113.6, 116.0, 120.2, 121.2, 121.4, 129.6, 129.7, 138.4, 139.9, 155.8, 159.0, 198.4; UV λ_{max} (MeCN) 218 nm (ε 29800 $M^{-1}cm^{-1}$), sh 200, 244, 276, 302 nm; IR (KBr; cm^{-1}) 3209 (br m), 2943 (w), 2925 (w), 2852 (w), 1668 (s), 1581 (s), 1495 (m), 1438 (w), 1363

(m), 1285 (s), 1212 (m), 1156 (m), 1034 (s), 879 (m), 789 (s), 690 (m), 603 (w); MS, m/e (I): 256 (20), 121 (100), 103 (10), 91 (15), 77 (18), 65 (6); Exact Mass Calcd. for $C_{16}H_{16}O_3$: 256.1099. Found: 256.1094; Anal.: Calcd $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.17; H, 6.31.

4-[2-(3-methoxyphenyl)ethoxy]acetophenone (**5b**). In an oven-dried 50 mL round-bottom flask was added 1-tosyl-2-(3-methoxyphenyl)ethane (2.99 g, 0.01 mol) and 4-hydroxy acetophenone (1.23 g, 0.09 mol). The mixture was dissolved in 30 mL freshly distilled acetone, after which anhydrous potassium carbonate (1.32 g, 0.0955 mol) was added. The resulting yellow mixture was gently refluxed until the tosylate was consumed as monitored by ^{1}H NMR spectroscopy (several days). The solution was filtered, concentrated under reduced pressure and acidified with dilute HCl (3 M, 20 mL). Addition of ether (15 mL) caused precipitation of salts, and after separation the organic layer was dried with magnesium sulfate, filtered and concentrated under reduced pressure. Recrystallization of the resulting pink solid was accomplished from 20% diethyl ether in hexanes to yield **5b** as colorless crystals (0.3 g, 0.0011 mol, 12%): mp. 69.5-70.7°C; ^{1}H NMR ($CDCl_3$) δ 2.53 (s, 3H), 3.08 (t, J = 7.0 Hz, 2H), 3.79 (s, 3H), 4.22 (t, J = 7.0 Hz, 2H), 6.80-6.92 (m, 5H), 7.23 (m, 1H), 7.89 (d, J = 1.4 Hz, 2H); ^{13}C NMR δ ($CDCl_3$) 26.3, 35.7, 55.2, 68.8, 111.9, 114.2, 114.9, 121.3, 129.5, 130.4, 130.6, 139.4, 159.8, 162.7, 196.8; UV λ_{max} (MeCN) 196 nm (ε 26000 $M^{-1}cm^{-1}$), sh 216, 266 nm; IR (KBr; cm^{-1}) 2966 (w), 2915 (w), 2839 (w), 1680 (s), 1604 (s), 1473 (m), 1364 (m), 1316 (m), 1275 (s), 1170 (s), 1116 (w), 1018 (m), 830 (s), 797 (m), 699 (m), 593 (m); MS, m/e (I): 270 (15), 135 (100), 121 (8), 105 (12), 91 (10), 77 (10), 43 (18); HRMS: Calcd. for $C_{17}H_{18}O_3$: 270.1256. Found: 270.1253; Anal: Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.61; H, 6.80.

3-[2-(4-methoxyphenyl)ethoxy]acetophenone (**6b**). To 4-methoxyphenethyl bromide (0.63 g, 3.1 mmol) in 20 mL dry acetone was added 0.40 g (2.95 mmol) 3-hydroxyacetophenone and 0.41

g (2.95 mmol) anhydrous potassium carbonate. After reflux for 15 hours, the canary yellow solution was filtered, concentrated under reduced pressure and the residue extracted into diethyl ether (30 mL). The ether solution was washed with water (30 mL) and 3% aqueous HCl (30 mL), dried with sodium sulfate and stripped of solvent on the rotary evaporator. The product was recrystallized from ethanol/water, yielding colorless crystals of **6b** (0.08 g, 0.3 mmol, 10%): m.p. 46.3 - 47.7°C; ^{1}H NMR ($CDCl_3$) δ 2.56 (s, 3H), 3.04 (t, J = 7.0 Hz, 2H), 3.78 (s, 3H), 4.17 (t, J = 7.0 Hz, 2H), 6.84 (m, 2H), 7.09 (m, 1H), 7.19 (m, 2H), 7.33 (t, J = 2.0 Hz, 1H), 7.49 - 7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 26.7, 34.8, 55.3, 69.1, 113.2, 113.9, 120.0, 121.1, 129.5, 129.9, 130.0, 138.5, 158.3, 159.1, 197.9; UV λ_{max} (MeCN) 196 nm (ε 20000 $M^{-1}cm^{-1}$), sh 216, 244, 280, 302 nm; IR (KBr; cm^{-1}) 2954 (w), 2936 (w), 2838 (w), 1678 (s), 1610 (m), 1580 (s), 1513 (s), 1443 (m), 1360 (m), 1282 (s), 1244 (s), 1213 (s), 1113 (w), 1027 (s), 892 (w), 867 (w), 819 (s), 784 (m), 683 (m); MS, m/e (I): 270 (12), 135 (100), 121 (50), 105 (7), 91 (7), 77 (7), 43 (7); HRMS: Calcd. for $C_{17}H_{18}O_3$: 270.1256. Found: 270.1253; Anal: Calcd $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.46; H, 6.69.

3-[2-(3-methoxyphenyl)ethoxy]acetophenone (**7b**). This compound was prepared in a similar fashion as **5b**, except that 3-hydroxyacetophenone (2.51 g, 18.4 mmol) was coupled to 1-tosyl-2-(3-methoxyphenyl)ethane (6.27 g, 20.5 mmol) in the presence of anhydrous potassium carbonate (2.89 g, 20.9 mmol). After 24 hours reflux, a second portion of anhydrous potassium carbonate (0.5 g, 3.6 mmol) was added and the reaction was complete after 48 hours. Isolation as above yielded crude **7b**, which was further purified by radial chromatography using chloroform followed by column chromotography using 30% ethyl acetate in hexanes as eluant. This yielded the product as a colorless oil which has not crystallized (3.2 g, 12 mmol, 65%): ^{1}H NMR ($CDCl_3$) δ 2.56 (s, 3H), 3.07 (t, J = 7.0 Hz, 2H), 3.79 (s, 3H), 4.21 (t, J = 7.0 Hz, 2H), 6.76-6.87

(m, 3H), 7.06 - 7.10 (m, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.34 (t, J = 7.9 Hz, 1H), 7.45-7.53 (m, 2H); ^{13}C NMR δ ($CDCl_3$) 26.7, 35.8, 55.2, 68.8, 111.9, 113.2, 114.8, 120.1, 121.1, 121.3, 129.5, 129.6, 130.3, 138.5, 159.0, 160.4, 197.9; UV λ_{max} (MeCN) 218 nm (ε 29800 $M^{-1}cm^{-1}$), sh 200, 244, 276, 302 nm; IR (KBr; cm^{-1}) 2964 (w), 2936 (w), 1678 (s), 1604 (s), 1580 (s), 1513 (s), 1443 (m), 1360 (m), 1283 (s), 1244 (s), 1113 (w), 1028 (s), 892 (w), 819 (s); MS, m/e (I): 270 (25), 135 (100), 121 (20), 105 (30), 91 (40), 77 (29), 65 (20), 43 (40); HRMS: Calcd. for $C_{17}H_{18}O_3$: 270.1256. Found: 270.1259. Anal: Calcd $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.89; H, 6.78.

References

(1) Fieser, L.F.; Fieser, M. *Reagents for Organic Synthesis*; John Wiley and Sons: New York, 1967.

(2) Bachmann, W.E.; Thomas, D.G. *J. Am. Chem. Soc.* **1942**, *64*, 94.

(3) Crispin, D.J.; Vanstone, A.E.; Whitehurst, J.S. *J. Chem. Soc. (C)* **1970**, 10.

(4) Collins, D.J.; Fallon, G.D.; Skene, C.E. *Aust. J. Chem.* **1992**, *45*, 71.

Figure 1. Triplet-triplet absorption spectra of compounds **5a,b** in deoxygenated acetonitrile solution at 23.0 ± 0.1 ^{o}C.

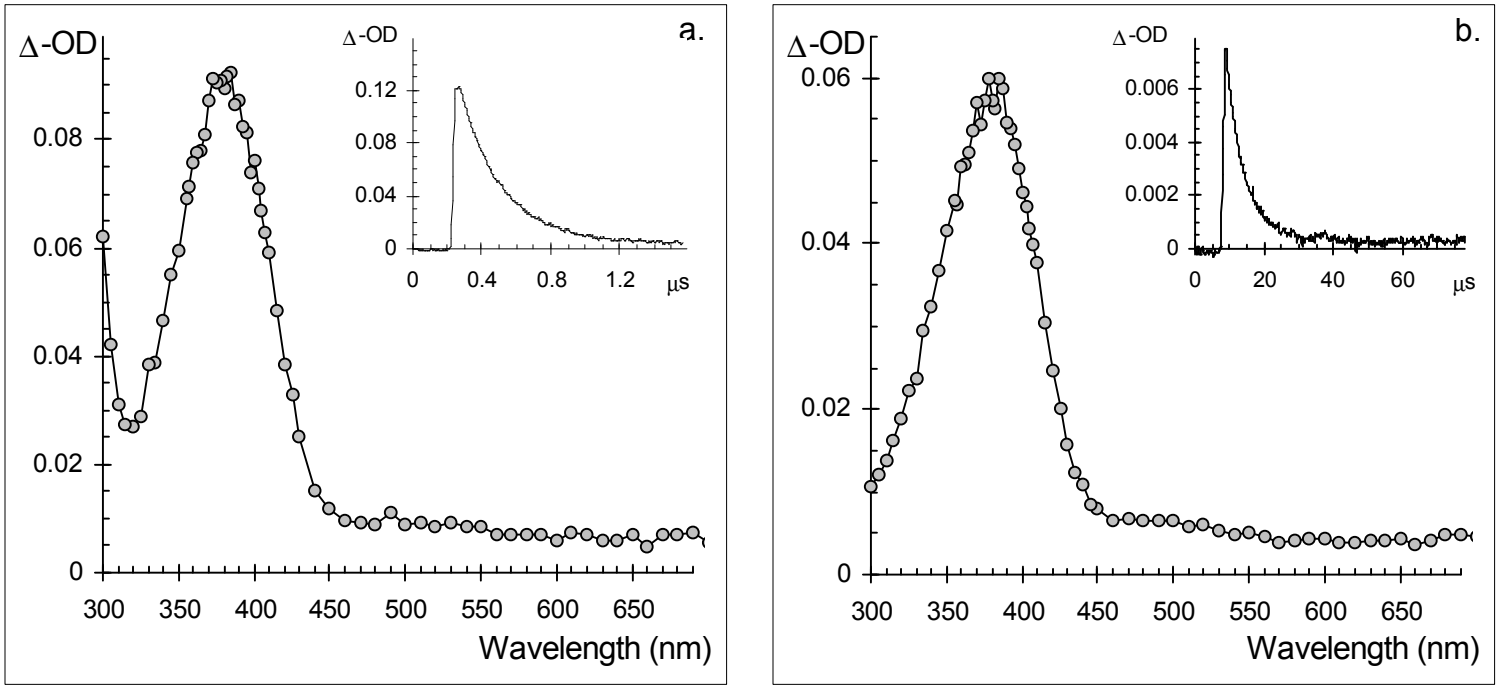

Figure 2. Triplet-triplet absorption spectra of compounds **6a,b** in deoxygenated acetonitrile solution at 23 ± 0.1 ^{o}C.