Supplementary Material

Strongly UV Absorbing Bifunctional Azoalkanes: Slow Intramolecular Singlet Energy Transfer, Induced Decomposition, and Fluorescent End Group Tagging of Polymers

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Experimental

General. The instruments employed have been described previously.[1] GC conditions: Hewlett Packard 5890A, HP-5 capillary column 30 m x 0.25 mm 80 °C for 5 min then 20 °C /min to 250 °C, injector and detector 230 °C. HPLC conditions: 10 mm x 25 cm Ultrasphere C_{18}, eluent 30% MeOH, 70% EtOAc.

2-(1-anthracenyl)-2-propanol To a solution of 1-acetylanthracene (4.4 g, 20 mmol) in anhydrous ether (70 mL) was added MeMgI (3 M in ether, 1.5 eq) dropwise at room temperature. After stirring the mixture for 2 h, dilute HCl (1 M, 5 mL) was added to dissolve the solid. The organic layer was separated and washed with water, then aqueous $NaCO_3$, and it was finally dried over $MgSO_4$. Removal of the solvent afforded 4.2 g of product, which was used in the next step without further purification. This reaction was repeated using 4.1 g of 1-acetylanthracene and the product was purified by silica gel column chromatography, eluting with 50/50 v/v CH_2Cl_2 in hexanes. Starting material (1.51 g) was recovered and 2.15 g of the product alcohol[2] was collected as an oil. ^{1}H NMR: 9.429 (1H, s), 8.429 (1H, s), 8.060 (1H, m), 7.974 (1H, m), 7.928 (1H, br. d), 7.536 (1H, br. d), 7.466 (2H, m), 7.367 (1H, dd), 1.936 (6H, s). ^{13}C NMR 143.318, 133.336, 131.331, 131.017, 129.307, 129.237, 129.142, 127.721, 127.336, 126.870, 125.853, 125.489, 124.424, 122.385, 74.591, 31.783.

2-(1-anthracenyl)-2-aminopropane The above crude alcohol (4.2 g) was dissolved in CH_2Cl_2 (30 mL) and sulfuric acid (30 mL, 58%) was added at 0 °C. With the

suspension maintained at 0 °C, sodium azide (4.0 g) was added portionwise. The mixture was then warmed to room temperature and stirred overnight. The organic layer was separated, washed with aqueous $NaHCO_3$ then brine, and dried over $MgSO_4$. TLC (80:20 v/v CH_2Cl_2/hexane) of the crude mixture showed new spots for desired product (R_f ~ 0.3) and 1-isopropenylanthracene (R_f ~ 1). The crude mixture was reduced at room temperature by dissolving it in anhydrous ether (80 mL) and adding $LiAlH_4$ (1.8 g) portionwise with stirring over 2 h. The mixture was refluxed for 2 h more, and water was added cautiously to destroy unreacted $LiAlH_4$. The precipitate was filtered off and washed with ether at least three times. After solvent removal from the combined ether solutions, the residue was purified by silica gel column chromatography eluting with 80/20 v/v CH_2Cl_2 /ether. The product amine (2.13 g oil) was obtained in 45.3% yield for three steps. ^{1}H NMR: 9.483 (1H, s), 8.434 (1H, s), 8.066 (1H, m), 7.970 (1H, m), 7.907 (1H, d), 7.570 (1H, d), 7.460 (2H, m), 7.375 (1H, dd), 1.860 (6H, s), 1.826 (2H, s br.). ^{13}C NMR: 144.698, 133.590, 131.060, 130.893, 129.546, 129.260, 128.706, 127.690, 127.469, 127.084, 125.766, 125.410, 124.639, 122.396, 54.418, 33.553.

N-2-(1-anthracenyl-2-propyl)-N'-t-butylsulfamide2-(1-anthracenyl)-2-amino-propane (0.96 g, 4.08 mmol) and triethylamine (2.3 mL) were added to THF (25 mL). At room temperature, t-butyl sulfamyl chloride (30 mL of a solution containing 30 mmol in 75 mL of 1:1 v/v THF/hexanes) was added dropwise over 1 h.[1] The mixture was stirred overnight at room temperature, diluted with CH_2Cl_2 (50 mL), and NaOH (5 mL, 1 N) was added. The organic layer was separated, washed with water and dried over $MgSO_4$. After removing the solvents, the brown solid was purified by silica gel column chromatography (90/10 v/v CH_2Cl_2/ether). The yield of pure sulfamide (1.12 g) was 74.2%, m.p. 172-174 °C. ^{1}H NMR: 9.375 (1H, s), 8.468 (1H, s), 8.073 (1H, m), 7.981 (2H, m), 7.490 (4H, m), 4.753 (1H, s), 3.816 (1H, s), 2.100 (6H, s), 1.086 (9H, s). ^{13}C NMR: 139.966, 133.292, 131.413, 130.990, 129.867, 129.126, 128.969, 127.952, 127.732, 126.096, 125.918, 125.654, 124.505, 124.150, 60.246, 54.744, 30.206, 29.903.

N-(1-anthracenyl-2-propyl)-N'-t-butyldiazene The above sulfamide (0.38 g, 1 mmol) was added to 30 mL of dry ether containing 200 mg of NaH (50% in mineral oil, washed with hexanes before use).[3] The suspension was stirred at room temperature for 3 h, then it was cooled to -30 °C. t-Butyl hypochlorite (216 mg, 2 equiv.) was added by syringe and the mixture was kept below -20 °C for at least 20 min. After warming to room temperature, the mixture was stirred overnight, and water (2 mL) was added. The ethereal solution was separated, washed with brine and dried over $MgSO_4$. Removal of solvent afforded a light-sensitive product which was purified by silica gel chromatography on a column wrapped with aluminum foil (20:80 CH_2Cl_2:hexanes). Yield: 158 mg of yellow oil. ^{1}H NMR: 8.436 (1H, s), 8.278 (1H, s), 7.935 (3H, m), 7.639 (2H, dd), 7.465 (3H, m), 1.849 (6H, s), 1.209 (9H, s). ^{13}C NMR: 143.252, 133.445, 130.808, 129.105, 128.772, 127.966, 127.819, 127.207, 127.086, 126.788, 125.601, 125.383, 124.778, 123.887, 73.129, 67.312, 27.669, 26.791.

1-(2-propenyl)anthracene was isolated as a byproduct of the reaction of 2-(1-anthracenyl)-2-propanol with hydrazoic acid (see above). Purification by silica gel column chromatography (5% CH_2Cl_2 in hexane) afforded an oil whose ^{1}H NMR spectrum matched the one published.[4] ^{1}H NMR 8.603 (1H, s), 8.415 (1H, s), 7.977 (2H, m), 7.908 (1H, d), 7.426 (3H, m), 7.249 (1H, d), 5.484 (1H, s), 5.165 (1H, s), 2.285 (3H, s). ^{13}C 145.006, 142.468, 132.224, 131.814, 131.644, 129.643, 128.779, 128.114, 127.657, 126.736, 125.695, 125.474, 125.115, 124.780, 123.844, 116.429, 25.403.

1-Isopropylanthracene. Attempts to hydrogenate 1-(2-propenyl)anthracene catalytically gave partial reduction of the aromatic system. Therefore 2-(1-anthracenyl)-2-propanol (0.27 g, 1.1 mmol) was reduced directly to the hydrocarbon by adding it to 15 mL of anhydrous ether followed by addition of $ZnBr_2$ (0.56 g, 2.4 mmol) and $NaBH_3CN$ (0.23 g, 3.6 mmol).[5] After refluxing for 3 days with GC monitoring, 1M HCl (20 mL) was added to destroy the excess reagents. The aqueous layer was separated and extracted 2x with ether. The combined ether layers were washed with water and dried over $MgSO_4$.

Concentration under vacuum left a gelatinous residue that was purified by silica gel column chromatography (hexane). The yield was 0.185 g (73.5%) of oily 1-isopropylanthracene that showed only one GC peak. ^{1}H NMR 8.673 (1H, s), 8.426 (1H, s), 8.001 (2H, m), 7.860 (1H, d), 7.434 (4H, m), 3.919 (1H, sept), 4.75 (6H, d). ^{13}C NMR: 144.743, 132.527, 131.696, 131.320, 130.234, 128.849, 128.021, 126.807, 125.556, 125.426, 125.388, 122.279, 121.053, 28.974, 23.748.

2-(2-anthracenyl)-2-propylamine Under argon, anhydrous $CeCl_3$ (8.1 g, 20 mmol) was suspended in THF (120 mL) in an ice bath. The mixture was warmed to room temperature, stirred for one h, and cooled to -78 °C. MeLi (1.6 M, 6 mL in ether) was added dropwise while keeping the temperature below –65 °C.[6] After stirring the yellow solution for 2 h, 2-cyanoanthracene (1.0 g, 5.0 mmol)[7] in THF (20 mL) was then added by syringe over the course of 20 min. The stirring was continued for 4 h; then the temperature was raised to –20 °C and conc. NH_4OH (15 mL) was added. After warming the mixture to room temperature, the reaction mixture was filtered to remove solid cerium salts, which were washed with THF. The washings were combined with the filtrate and the solution was evaporated. The residue was acidified in 2N HCl and the insoluble amine hydrochloride was collected and washed sequentially with 2N HCl, brine, and ether. The solid was then suspended in NaOH (2N) and stirred for one h. The solid amine was filtered and washed with aq. NaOH then brine. After drying, the solid was dissolved in $CHCl_3$ and filtered to remove any insoluble impurities. Removal of the solvent afforded 0.61 g of the amine, mp 102- 104 °C (dec.) To recover more product, the HCl washes were neutralized with aq. NaOH and extracted with ether. Removal of the ether gave another 0.1 g of amine. ^{1}H NMR 8.39 (2H, d), 7.80 (4H, m), 7.62 (1H, dd), 7.45 (2H, m), 1.69 (2H, br s), 1.62 (6H, s). ^{13}C NMR 147.126, 132.121, 131.815, 131.767, 130.725, 128.404, 128.369, 128.311, 126.492, 125.904, 125.473, 125.341, 124.544, 122.099, 52.822, 32.594.

N-2-(2-anthracenylpropyl)-N'-t-butylsulfamide A solution of t-butanol (1.7 g, 22.5 mmol) in hexanes (25 mL) was flushed with argon. At room temperature, chlorosulfonyl isocyanate (2 mL, 3.1 g, 22.5 mmol) was then added slowly under argon; then the mixture was warmed to 45 °C for 1 h. The resulting cloudy solution of t-butylsulfamyl chloride was diluted with THF until it was clear. In another flask, triethylamine (2.7 g, 2.7 mmol), and 2-(2-anthracenyl)-2-propylamine (2.0 g, 8.6 mmol) were dissolved in THF (15 mL). To this amine solution, the t-butylsulfamyl chloride solution was added dropwise under argon. The reaction mixture was stirred at room temperature overnight. The suspension was diluted with chloroform (50 mL) and washed successively with HCl (1 M), saturated Na_2CO_3, and water. Drying over $MgSO_4$ and removal of solvent gave 1.8 g crude sulfamide (mp 173 -175 °C), which was used directly in the next step. ^{1}H NMR 8.40 (1H, br s), 8.43 (1H, br s), 8.01 (4H, m), 7.63 (1H, dd), 7.47 (2H, dd), 4.61 (1H, br s), 3.80 (1H, br s), 1.89 (3H, s), 1.26 (9H, s). ^{13}C NMR 142.588, 134.423, 134.341, 132.204, 131.336, 128.756, 128.336, 127.816127.447, 126.969, 126.002, 125.716, 124.357, 124.054, 58.718, 54.633, 30.152, 29.278

2-(2-anthracenyl)-2-propylazo-t-butane The sulfamide (0.70 g, 1.87 mmol) was suspended in NaOH (8 eq. 15 mmol in 30 mL of water) and cooled to 0 °C. Sodium hypochlorite (bleach, 35 mL, 5.25% in water) was added dropwise at 0 °C over 20 min and the mixture was stirred at room temperature overnight. The precipitate was collected and dissolved in CH_2Cl_2. The solution was washed with water and dried over $MgSO_4$. Removal of solvent and silica gel column chromatography (hexanes: CH_2Cl_2 3:1) afforded 0.315 g pure azoalkane product (55.4%). m.p. 131°C (dec.) ^{1}H NMR 8.39 (2H, br d), 7.98 (4H, m), 7.44 (3H, m), 1.59 (6H, s), 1.26 (9H, s). ^{13}C NMR 143.425, 132.037, 131.885, 131.820, 130.893, 128.373, 128.337, 128.132, 126.622, 125.939, 125.431, 125.367, 125.353, 124.308, 71.238, 67.050, 27.062, 26.447. Anal: calc. for M+H 305.20177, found 305.20154.

2-t-Heptylanthracene was isolated by preparative TLC from the irradiation of **2**. ^{1}H NMR (0.927 s, 9H), 1.496 (s, 6H), 7.420 (dd, 2H), 7.753 (dd, 1H), 7.871-8.002 (m, 4H), 8.371 (s, 1H), 8.398 (s, 1H).

2-Isopropenylanthracene[2] was made from 2-acetylanthracene by the Wittig reaction according to the literature.[4]

2-Isopropylanthracene[2] was prepared by reduction of 2-(2-anthracenyl)-2-propanol using $NaBH_3CN$ and $ZnBr_2$ as in the case of the 1-isomer.[5]

Thermolysis Kinetics were carried out using a solution of 29 mg of **1** or **2** plus 40 mg thiophenol in 1 mL 1-methylnaphthalene in our constant volume, variable pressure kinetics apparatus.[1]

Polymerization of Styrene with 1 and **2.** A solution of 0.04 M **1** in 0.5 mL styrene and 0.75 mL benzene was heated at 105 ^{o}C for 4 h. The polymer was precipitated with methanol, redissolved in benzene, and reprecipitated twice more. After careful vacuum drying, the absorption and fluorescene spectra were determined in toluene. A similar procedure was followed for **2** as initiator except the temperature was 90 ^{o}C and the time was 3.5 h

Polymerization of Methyl Methacrylate. Initiator **1** (15 mg), methyl methacrylate (0.5 mL), and C_6D_6 (0.75 mL) were sealed in a pyrex tube under vacuum. The solution was maintained at 62 ^{o}C and photolyzed at 313 nm for 2 h. The tube was opened and the solution was poured into 10 mL of methanol. The precipitate was collected and washed with methanol three times. The solid was dissolved in CH_2Cl_2 (1 mL) and poured into 10 mL of methanol again. The precipitate was collected, washed with methanol (4 x 1 mL) and dried under vacuum overnight.

Theoretical Calculations. Density functional theory calculations of bond dissociation energies (Table 3) and spin densities of radicals **3** and **7** were carried out using Gaussian 98 with the B3LYP/6-31G* basis set.[8]

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