

Supplementary data

The intrinsic photoferroelectric effect in the smectic C*-phase of a chiral azobenzene

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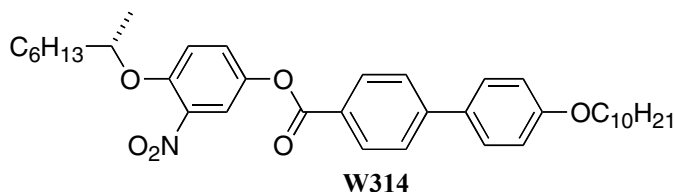
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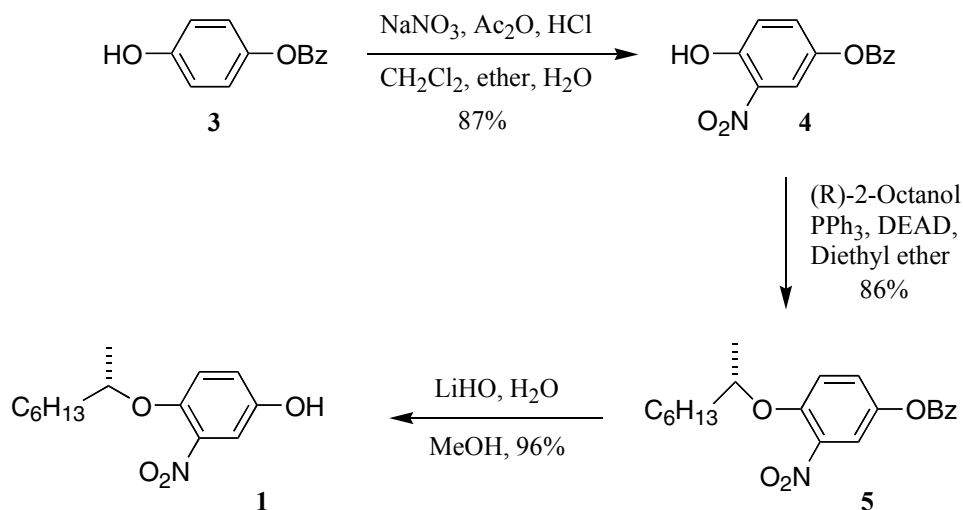
Synthesis of W470

Synthesis of nitrophenol 1

Synthesis of nitrophenol **1** was first accomplished in the context of synthesis of **W314**, the “parent” compound of azobenzene **W470** [Walba, D. M.; Ros, M. B.; Clark, N. A.; Shao, R.; Robinson, M. G.; Liu, J.-Y.; Johnson, K. M.; Doroski, D. *J. Am. Chem. Soc.* **1991**, *113*, (14), 5471-5474.]



Experimental details for the synthesis used for preparation of **W470**, as shown in **Scheme 1**, are given below.



Scheme 1

4-Hydroxy-3-nitrophenylbenzoate (4): To a solution of 4-hydroxyphenylbenzoate (**3**, commercially available from Alfa Aesar – www.alfa.com) (10g, 0.04672 mol), NaNO_3 (4.17g, 0.04906 mol), H_2O (56mL), CH_2Cl_2 (94mL), and Ether (188mL), was carefully added concentrated HCl (11 mL) and the mixture was stirred vigorously. A catalytic amount of acetic anhydride (1.25mL) was then added and the reaction was allowed to stir overnight. The reaction mixture was transferred to a separatory funnel, washed with brine (1 x 250 mL) and the organic layer was dried over Na_2SO_4 . Evaporation of solvent yielded a yellow solid, which was recrystallized twice from ethanol to yield 8.62g (71%) of ester **4**.

^1H NMR (CDCl_3 , 400MHz) δ 7.22 (d, 1H, $J = 9.3\text{Hz}$), 7.44-7.70(m, 4H), 7.99 (d, 1H $J = 2\text{Hz}$), 8.17(dd, 2H, $J = 1.2, 7.2\text{Hz}$), 10.51 (s, 1H), ^{13}C NMR (CDCl_3 , 125.83MHz) 117.0, 117.9, 128.4, 128.5, 128.9, 130.1, 130.2, 130.6, 133.7, 136.0, 146.6, 149.2, 164.0.

(S)-4-1-Methylheptyloxy-3-nitro-phenylbenzoate (5): Diethyl-azodicarboxylate (DEAD) (3.0 mL, 0.012 mol) was added via syringe with stirring under argon to a solution of phenol **4** (2.10 g, 0.008 mol), triphenylphosphine (3.16 g, 0.012 mol), and (R)-2-octanol (1.10 mL, 0.012 mol) in 150 mL of anhydrous ether. The reaction mixture was stirred overnight at room temperature. The reaction was quenched with 30% H_2O_2 (3

mL) to oxidize the excess triphenylphosphine. Water was then added and the organic layer was separated and washed with brine. The organic layer was dried over anhydrous MgSO₄ and concentrated via rotary evaporation. The crude product was purified by flash chromatography (90:10 Hexanes:EtOAc) to give 2.60 g (86%) of the ether **5**.

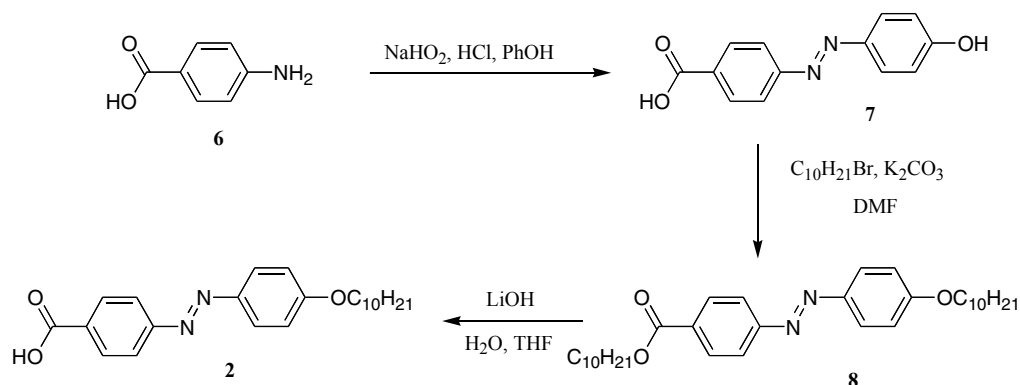
¹H NMR (CDCl₃, 500MHz) δ 7.90 (d, 2H, *J* = 8.0Hz), 7.40(m, 2H), 7.24 (t, 2H *J* = 7.5Hz), 7.11(dd, 1H, *J* = 10.0, 3.0Hz), 6.82(d, 1H *J* = 9Hz), 4.22 (sextet, 1H), 1.50(m, 1H, 1.1-1.2(m, 12H), 0.6(t, 3H). ¹³C NMR (125.83MHz, CDCl₃) 14.0, 20.4, 23.1, 24.1, 30.3, 32.5, 37.5, 73.0, 115.5, 117.1, 128.1, 128.4, 128.5, 130.1, 130.2, 130.6, 133.7, 134.5, 145.6, 150.7, 164.0.

(S)-4-(1-Methylheptyloxy)-3-nitrophenol (1): The phenylbenzoate **5** (2.6 g, 7.0 mmol) was dissolved in 10 mL methanol, and distilled water was added until the solution remained milky yellow with vigorous stirring. An excess of lithium hydroxide monohydrate (2.0 g, 47 mmol), was then added. The resulting dark red mixture was stirred at room temperature for 8 hours and quenched with concentrated HCl until pH=2. The reaction was extracted with CH₂Cl₂ and the organic layer was separated; washed with sat. NaHCO₃, followed by brine, and dried over MgSO₄. The solvent was evaporated and the crude product was purified by flash chromatography (90:10 to 50:50 Hexanes:EtOAc), to yield phenol **1** (1.8 g, 96% yield).

¹H NMR (CDCl₃, 500MHz) δ 7.30 (d, 2H, *J* = 8.0Hz), 7.40(m, 2H), 6.98(dd, 2H, *J* = 10.0, 3.0Hz), 5.81(s, 1H), 4.21 (sextet, 2H), 1.56(m, 2H), 1.5(m, 2H), 1.1-1.3(m, 23H), 0.8(t, 6H). ¹³C NMR (125.83MHz, CDCl₃) 14.0, 20.4, 23.1, 24.1, 30.3, 32.5, 27.5, 73.0, 111.4, 116.5, 122.4, 135.5, 146.5, 149.8.

Synthesis of azobenzene carboxylic acid **2**.

Experimental details of the synthesis of azobenzene carboxylic acid **2**, as shown in **Scheme 2**, are given below.



Scheme 2

4-Hydroxy-4'-diazobenzoic acid (7): p-Aminobenzoic acid (**6**) (13.5 g, 0.0985 mol) was dissolved in 450mL of 6M HCl and cooled to 0°C. To this suspension a saturated solution of NaNO_2 (11.1 mL of 9.03 M solution, 0.0985 mol) was added slowly. This mixture was stirred for 30min. In another flask, phenol (9.16 g, 0.0985 mol) was dissolved in 10% NaOH solution and cooled to 0°C. The p-aminobenzoic acid solution was then poured all at once into the phenol solution. The reaction mixture turned to a deep red. This mixture was stirred for an hour and allowed to warm to room temperature slowly. Aqueous HCl was then added to acidify the solution to $\text{pH} = 2$. At this point an orange precipitate formed. The precipitate was collected by vacuum filtration, and the resulting solid was then dissolved in hot DMSO and passed through filter paper to remove additional impurities. Crude acid-phenol **7** was obtained after evaporation of the solvent and directly used to the next step of synthesis without further purification due to the difficulty of drying the product.

^1H NMR (DMSO- d_6 , 500MHz) δ 8.20(d, 2H, $J = 8.5\text{Hz}$), 7.91(dd, 4H, $J = 20.0, 9.0\text{Hz}$), 7.05(d, 1H, $J = 9\text{Hz}$). ^{13}C NMR (125.83MHz, DMSO- d_6) 116.0, 116.1, 122.6, 122.7, 124.1, 124.2, 130.4, 130.5, 132.8, 145.1, 157.7, 159.5, 172.0.

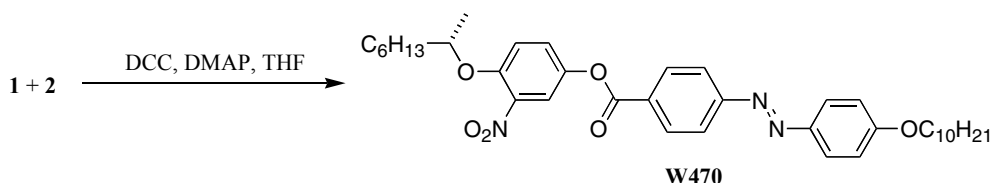
Decyl-(4-decyloxy-4'-azobenzoate) (8): The crude Acid-phenol **7** obtained as above, was dissolved in DMF (250mL), then n-decylbromide (22.7 mL, 0.11 mol), and anhydrous K₂CO₃(30.22 g, 0.219 mol) were added. The mixture was refluxed overnight and then cooled to room temperature. This mixture was filtered through Celite and then concentrated by rotary evaporation. Ether was added and this was washed twice with distilled water and once with brine. The organic layer was finally dried over MgSO₄. The solvent was evaporated by rotovap then purified by flash chromatography (90:10 Hexanes: EtOAc) to give 11.8 g (50% based on **6**) of crude ester-ether **8** as an orange solid. The solid was further purified by trituration with Hexanes.

¹H NMR (CDCl₃, 500MHz) δ 8.50 (d, 2H, *J* = 8.5Hz), 7.0 (dd, 4H, *J* = 15, 9Hz), 6.99(d, 2H, *J* = 9Hz), 4.322 (t, 2H), 4.03 (t, 2H), 1.7(m, 4H), 1.5 (m, 4H), 1.2-1.50(m, 1H, 1.1-1.2(m, 27H), 0.9(m, 5H). ¹³C NMR (125.83MHz, CDCl₃) 14.0, 14.1, 23.1, 23.2, 26.5, 26.6, 30.1, 30.3, 30.6, 32.5, 32.6, 66.3, 72.3, 114.5, 114.6, 122.6, 122.7, 123.3, 123.4, 130.0, 130.1, 123.7, 144.1, 156.8, 161.0, 167.0.

4-Decyloxy-4'-azobenzoic acid (2). Ether-ester **8** (5.4 g, 10.3 mmol), was dissolved in 500ml of 4:1 THF:H₂O. Lithium hydroxide monohydrate (2.60 g, 62.07 mmol) was then added and the mixture was refluxed overnight and THF was removed by rotovap. The aqueous residue was then acidified to pH = 2 with concentrated HCl. Some product precipitated out and this was collected by vacuum filtration. Extracting the aqueous solution with three portions of ether provided additional product. The combined crude acid **2**, obtained as an orange solid, was purified by recrystallization from EtOH to give 4.00 g (100%) of azobenzene **2**. Due to solubility problems, this material was characterized using mass spectroscopy: MS(EI) m/z (rel. intensity): 382.1(80), 271.9, 121.0, 107.0, 83.0, 69.0, 55.0, 43.0.

Synthesis of W470

Experimental details for synthesis of (S)-**W470**, as shown **Scheme 3**, are given below.



Scheme 3

The azobenzene acid **2** (4.3 g, 0.0162 mol) nitrophenol **1** (3.077 g, 0.0081 mol) and DMAP (3.37g, cat.) were dissolved in anhydrous CH₂Cl₂ (224 mL). Under argon atmosphere, (4.15g, 0.020mol) of a CH₂Cl₂ solution of DCC was added via syringe. This mixture was stirred under argon overnight and quenched with 5% HCl (10 mL). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂. The organic layers were combined and washed with brine, then dried over MgSO₄. The resulting crude product was purified by flash chromatography (92:8 Hexanes: EtOAc), to give 4.79g (96%) of **W470**.

¹H NMR (CDCl₃, 500MHz) δ 8.28 (d, 2H, *J* = 8.5Hz), 7.95 (m, 4H), 7.73 (d, 1H, *J* = 3.0Hz), 7.40 (dd, 1H, *J* = 10, 3Hz), 7.10 (d, 1H *J* = 9.5Hz), 1.65 (m, 1H), 1.25-1.5 (m, 26H), 0.89(t, 6H). ¹³C NMR (125.83MHz, CDCl₃) 164.69, 162.8, 156.24, 149.80, 147.06, 142.98, 140.69, 131.49, 129.78, 127.39, 125.57, 122.82, 119.32, 116.69, 115.06, 68.69, 36.44, 32.1, 31.9, 29.76, 29.5, 29.4, 26.21, 25.45, 22.8, 19.73, 14.3.

Mass Spectrum(EI+) *m/z*(rel. intensity): 631.4(55), 601.4, 419.2.

Analysis calc'd for C₃₇H₄₉N₂O₄: C 70.43; H 7.82; N 6.65; found: C 70.29, H 7.85, N 6.56.