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Binding of an Acetonitrile Molecule Inside the Ethereal Cavity of a Hexaarylbenzene-Based Receptor via a Synergy of C-H···O/C-H···π Interactions

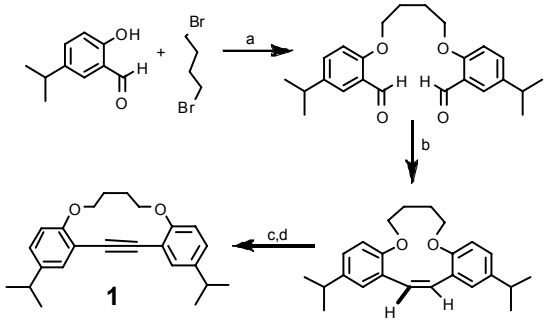
Ruchi Shukla, Sergey V. Lindeman, and Rajendra Rathore*

Marquette University, Department of Chemistry, P.O. Box 1881, Milwaukee, WI 53201-1881

General Experimental Details.

Anhydrous tetrahydrofuran (THF) was prepared by refluxing the commercial tetrahydrofuran (Aldrich) over lithium tetrahydroaluminate under an argon atmosphere for 24 hours followed by distillation. It was stored under an argon atmosphere in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. Dichloromethane (Aldrich) was repeatedly stirred with fresh aliquots of conc. sulfuric acid (~10 % by volume) until the acid layer remained colorless. After separation it was washed successively with water, aqueous sodium bicarbonate, water, and saturated aqueous sodium chloride and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from P_2O_5 under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. The hexanes and toluene were distilled from P_2O_5 under an argon atmosphere and then refluxed over calcium hydride (~12 hrs). After distillation from CaH_2, the solvents were stored in Schlenk flasks under argon atmosphere.

Scheme 1. Synthesis of bridged diarylacetylene **1**.



[a]NaOH/EtOH/reflux. [b]$TiCl_4$/Zn/Py/THF/reflux. [c]Br_2/AcOH. [d]KO*t*Bu/THF/22 °C.

Synthesis of 5-Isopropylsalicylaldehyde. Following a literature procedure,[S1] 4-isopropylphenol (27.2 g, 0.2 mol), anhydrous magnesium chloride (28.8 g, 0.3 mol), triethylamine (100 mL, 0.75 mol) in acetonitrile (150 mL) were mixed with

paraformaldehyde (30 g, 1.0 mol) in a 500-mL round bottom fitted with a condenser. The resulting mixture was refluxed for 12 h and cooled to room temperature and treated carefully with 300 mL of 5% hydrochloric acid. It was then extracted with dicloromethane (3 x150 mL) and the combined organic layers were dried over $MgSO_4$ and evaporated to give 5-isopropylsalicylaldehyde as viscous liquid in 91 % yield, which was used for next step without further purification. ^{1}H NMR ($CDCl_3$) δ: 1.32 (d, 6H), 2.84 (m, 1H), 6.9 (d, 2H), 7.3 (m, 2H), 9.86 (d, 1H) 10.86 (d, 1H); ^{13}C NMR ($CDCl_3$) δ: 24.15, 33.25, 117.25, 120.49, 131.05, 135.92, 140.51, 160, 196.93.

Preparation of bis-2,2'-[1,4-butanediylbis(oxy)]-5-isopropylbenzaldehyde. Thus, following closely a literature procedure,[S2] an addition of 5-isopropylsalicylaldehyde (32.8 g, 0.2 M) to an ethanloic solution (200 mL) of potassium hydroxide (11.2 g, 0.2 mol) immediately resulted in a yellow precipitate of the potassium salt of salicylaldehyde which dissolved upon further refluxing. 1,4-Dibromobutane (0.095 mol) was added drop wise to the above reaction mixture and the resulting mixture was refluxed for additional 8 h. Upon cooling the resulting mixture just below the boiling point of ethanol and a rapid filteration produced a clear solution which upon standing at room temperature produced a mass of pale yellow crystals. The crystallanie mass was filtered and washed with a mixture of cold ethanol and water (1;1, 50 mL). Another re-crystallization of the resulting solid from ethanol afforded colorless crystalline bis-2,2'-[1,4-butanediylbis(oxy)]-5-isopropylbenzaldehyde in 89% yield; mp 94-96 ^{o}C; ^{1}H NMR ($CDCl_3$) δ: 1.2 (d, 12H), 2.0 (m, 4H), 2.8 (m, 2H), 4.15 (m, 4H), 6.93 (d, 2H), 7.42 (dd, 2H), 7.68 (d, 2H), 10.5 (d, 1H); ^{13}C NMR ($CDCl_3$) δ: 24.00, 26.00, 33.22, 67.95, 112.47, 124.51, 125.76, 134.41, 141.20, 159.61, 189.87. GC-MS *m/z* 384 (M^+), 382 calcd for $C_{24}H_{34}O_4$.

Preparation of cis/trans Stilbene.[S3] To chilled (~0 ^{o}C) anhydrous tetrahydrofuran (1 L) was added $TiCl_4$ (30 ml, 270 mmol) drop wise with the aid of a dropping funnel under an atmosphere. To the resulting mixture was added Zn dust (22 g, 340 mmol) and dry pyridine (1 g, 13 mmol) and solution was warmed to room temperature. The black suspension thus obtained was refluxed for two hours. A solution of dialdehyde from above (15 g, 39 mmol) in THF (500 mL) was added drop wise to this black reaction mixture during a course of 72 h while refluxing. The resultant mixture was cooled to room temperature and quenched with 10% aqueous K_2CO_3 (300 mL). The organic layer was separated and the aqueous suspension was extracted with dichloromethane (5 x 150 mL) followed by diethyl ether (3 x 100 mL). The combined organic layers were dried over anhydrous MgSO4, filtered and evaporated to afford syrupy liquid which was purified by flash chromatography on silica gel using 2:8 mixture of ethyl acetate and hexanes to afford a 1:1 mixture of *cis/trans* stilbenes in ~1:1 ratio as a viscous oil. Yield (85%). ^{1}H NMR ($CDCl_3$) δ: 0.9 (d, 4H), 1.1(d, 8H), 1.6 (m, 2H), δ1.9 (m, 2H), 2.6 (m, 2H), 3.90 (m, 4H), 6.4-7.2 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ: 24.00, 24.26, 24.37, 25.78, 26.01, 33.29, 33.71, 69.76, 71.97, 115.14, 118.51, 125.48, 126.16, 128.40, 128.66, 128.84, 129.63, 129.80, 141.01, 143.33, 153.50, 155.87. GC-MS *m/z* 350 (M^+), 350 calcd. for $C_{24}H_{30}O_2$.

Preparation of Diarylalkyne 1. To a solution of stilbene mixture (10 g, 28 mmol) in acetic acid (50 mL) was added drop wise a solution of bromine (4.8 g, 30 mmol) in acetic acid (20 mL). The reaction mixture was stirred at room temperature for 30 min and was poured in water (250 mL). The resulting mixture was extracted with dichloromethane (3 x 100 mL),

washed with aqueous sodium bisulfite (2 x 50 mL) and dried over anhydrous $MgSO_4$. Evaporation of solvent afforded a quantitative yield of the corresponding dibromostilbene which was used in the next step without further characterization or purification as follows.

A solution of dibromostilbene (14.2 g) in dry THF (200 mL) was added, in portions, potassium *t*-butoxide (8.4 g, 75 mmol). The resulting mixture was stirred at room temperature for 4 h and the progress of the reaction was monitored by TLC (10:90 ethyl acetate : hexanes). An standard aqueous workup and purification by flash chromatography on silica gel, using 10:90 mixture of ethyl acetate:hexanes as eluent, afforded pure diarylacetylene **1** as a viscous oil in >80% yield. ^{1}H NMR ($CDCl_3$) δ: 1.2 (d, 12H), 2.0 (m, 4H), 2.9 (m, 2H), 4.2 (m, 4H), 6.85 (d, 2H), 7.1 (dd, 2H), 7.3 (d, 2H); ^{13}C NMR ($CDCl_3$) δ: 24.25, 26.72, 33.49, 71.43, 91.83, 115.06, 116.27, 127.84, 129.36, 142.35, 159.41. GC-MS *m/z* 348 (M^+), 348 calcd. for $C_{24}H_{28}O_2$.

Preparation of 2 and 3 by Trimerization of Diarylacetylene 1. Diarylalkyne **1** (2 g, 5.8 mmol) was mixed with $Co_2(CO)_8$ (50 mg) in an oven dried Schlenk flask under an argon atmosphere and the flask was evacuated and filled with argon repeatedly (3 times). Anhydrous dioxane (50 mL) was added with the aid of a syringe and the resulting mixture was refluxed overnight. The dark colored mixture was then cooled to room temperature and was treated with 10% hydrochloric acid solution. The mixture was extracted with dichloromethane (3 x 50 mL) and the combined organic layers were dried over anhydrous Mg SO_4 and evaporated. A chromatographic separation of the resulting mixture on silica gel using a 10:90 mixture of ethyl acetate:hexanes as eluant, afforded starting acetylene **1** (1.45 g), trimer **3** (0.3 g), and the desired trimer **2** (0.16 g). The spectral data of **2** and **3** are summarized below:

3: Mp >300 ^{o}C; ^{1}H NMR ($CDCl_3$) δ: 0.9 (m, 36H), 1.9 (m, 12H), 2.25 (m, 6H), 3.8 (m,12 H), 6.15 (2 d, 6H), 6.5 (m, 6H), 6.75 (3d, 6H); ^{13}C NMR ($CDCl_3$) δ: 24.23, 24.29, 24.49, 24.61, 26.82, 26.98, 27.21, 31.82, 33.30, 67.68, 67.96, 108.25, 108.71, 109.63, 123.79, 124.15, δ124.48, 130.25, 130.49, 130.70, 130.78, 131.65, 137.60, 137.94, 138.02, 138.74, 153.11, 153.26, 153.78. FAB: *m/z* 1045 (M^+), 1045 calcd. for $C_{72}H_{84}O_6$.

2: ^{1}H NMR ($CDCl_3$) δ: 0.9 (d, 36H), 1.8 (br, 12H), 2.4 (sym m, 6H), 3.6 (br, 6H), 3.9 (br, 6H), 6.2 (d, 6H), 6.55 (sym m, 6H), 6.66 (d, 6H); ^{13}C NMR($CDCl_3$) δ: 24.32, 24.54, 26.65, 33.32, 68.03, 110.64, 124.25, 130.85, 131.52, 138.19, 138.34, 154.02. FAB: *m/z* 1045 (M^+), 1045 calcd. for $C_{72}H_{84}O_6$.

References

(S1) Hofslokken, N.U.; Skattebol, L. *Acta Chem. Scand.* **1999**, *53*, 258-262.

(S2) Simonis, U.; Walker, F.A.; Lee, P.L.; Hanquet, B.J.; Meyerhoff, D.J.; Scheidt, R. *J. Am. Chem. Soc.* **1987**, *109*, 2659-2679.

(S3) For a similar procedure, see: Rives, J.T.; Oliver, M.A.; Fronczek, F.R.; Gandour, R.D. *J. Org. Chem.* **1984**, *49*, 1627-1634.