Pergamon

SCIENCE DIRECT®

Tetrahedron Letters 44 (2003) 1215–1219

TETRAHEDRON LETTERS

Stereocontrolled synthesis of anthracene β-*C*-ribosides: fluorescent probes for photophysical studies of DNA

Robert S. Coleman* and Mark A. Mortensen

Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, OH 43210, USA

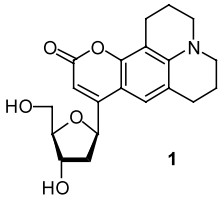
Received 13 September 2002; revised 6 December 2002; accepted 9 December 2002

Abstract—Effective, stereocontrolled syntheses of the 1-anthracenyl and 2-anthrancenyl β-*C*-2′-deoxyribosides are reported and were based on a diastereofacialselective, palladium-catalyzed glycosidation of the corresponding protected (4*S*,5*R*)-4-hydroxy-5-(hydroxymethyl)dihydrofuran.

1. Introduction

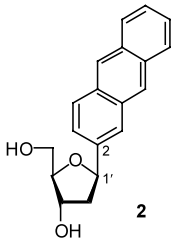
In studying the dynamic properties of DNA using ultrafast photophysical techniques,[1] it is necessary to appropriately localize a reporter molecule within the double helix. The native purine and pyrimidine bases have excited state lifetimes on the sub-picosecond time scale, which makes them unsuitable for studying dynamic events that occur on the picosecond or slower time-scale.[2] In our collaborative effort to understand molecular origins of the unique dynamics of DNA, we use an adaptation of the time-resolved Stokes shift technique[3] for measurement of the local structural relaxation in response to the instantaneously altered dipole moment in the excited state. As the nearby components of the DNA molecule relax, the electric field at the dipole is increased, resulting in a lowered energy of the probe molecule and an accompanying red-shift of the fluorescence.[4] The time dependence of the shift in the fluorescence can be related with the time-dependent relaxation the surrounding charged groups (i.e., the bases and sugar-phosphate backbone of DNA).

Our previous studies relied on coumarin *C*-riboside **1**[5] that is incorporated synthetically into DNA oligomers. This molecule is placed in the complementary position to a tetrahydrofuran abasic site analog.[6] This molecule is a dipolar probe, where the excited state is a charge transfer transition.[7] This probe has proven effective in time-resolved Stokes shift experiments with duplex DNA.[8,9]

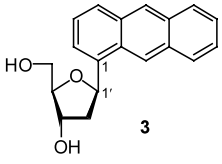


1

We propose that anthracene β-*C*-2′-deoxyribosides[10] will function as van der Waals probes. There will be a change in polarizability[11] upon excitation of these molecules[12] to the π* state, thereby altering van der Waals attractions for nearby groups. This change will affect the nearby components of the DNA by what can best be described as a 'mechanical' effect. Modeling studies were ambiguous with respect to the site of covalent attachment of anthracene to the deoxyribose C1′, as it appeared that both C1 and C2 of anthracene could provide appropriate localization of the probe within the DNA double helix. We now report full synthetic details for the preparation of C-ribosides **2** and **3**, and improved syntheses of 1- and 2-hydroxyanthracene.



2



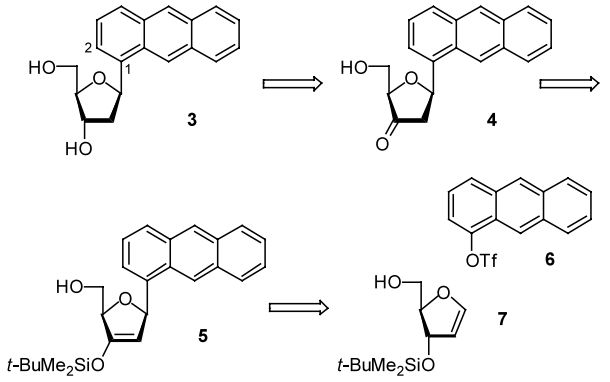
3

The synthesis of both probes used a reliable Heck coupling[13] between aryl triflate **6** and deoxyribose glycal **7**.[14] The resulting enol ether **5** was converted to

* Corresponding author. Tel.: 614-292-4548; fax: 614-292-4647; e-mail: coleman@chemistry.ohio-state.edu

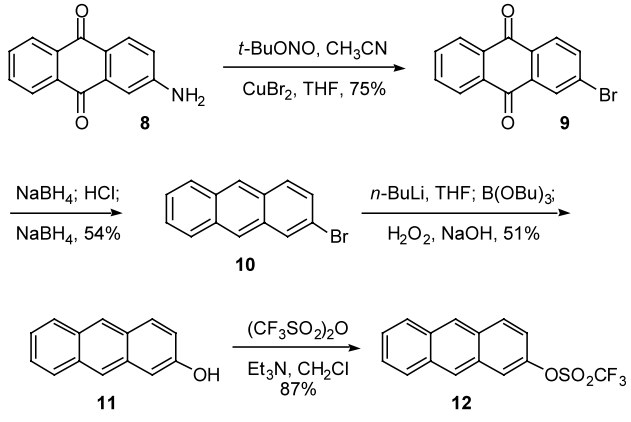
0040-4039/03/$ - see front matter
PII: S0040-4039(02)02791-0

ketone **4** by desilylation, either as a separate step or in the workup of the Heck coupling. The carbonyl group of **4** was reduced diastereoselectively to provide the 2′-deoxyribose system contained in **3**. The regioisomeric anthracene system **2** was constructed in an identical manner starting from 2-hydroxyanthracene. While the synthetic scheme for the synthesis of **2** and **3** is straightforward, it is far from trivial largely because the regioisomeric hydroxyanthracenes are difficult compounds to access, particularly the 2-hydroxy isomer.



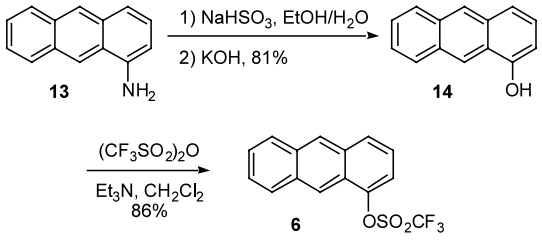
2. Synthesis of 1- and 2-hydroxyanthracene

The existing syntheses of 2-hydroxyanthracene or the corresponding anthraquinone are cumbersome or lengthy,[15] so we combined the more attractive aspects of several existing routes into a workable route to this phenol. 2-Aminoanthraquinone (**8**) proved to be a suitable starting material, and was converted to 2-bromoanthraquinone (**9**) by a Sandmeyer-like reaction. A solution of **8** in THF was added to a mixture of *tert*-butyl nitrite and cupric bromide in acetonitrile.[16] Only trace amounts of anthraquinone were observed as a side-product.



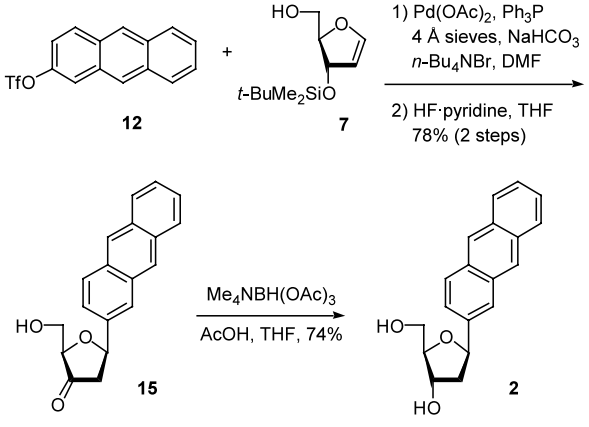
The quinone of **9** was reduced to the aromatic system by three-step sequence of reduction, elimination, and reduction[17] to afford 2-bromoanthracene (**10**). Conversion of the bromide of **10** to the corresponding phenol proceeded in modest yield via the intermediate anthracenyllithium species, which was trapped as the ditributyl borinate that was oxidized in situ to afford 2-hydroxyanthracene (**11**). Installation of the trifluoromethanesulfonate ester proceeded in high yield to afford coupling partner **12**.

Synthesis of the regioisomeric 1-hydroxyanthracene (**14**) proceeded uneventfully in good yield after optimization using a Bucherer reaction[18] of commercially available 1-aminoanthracene (**13**) to afford **14**. Installation of the trifluoromethanesulfonate ester under standard conditions proceeded in high yield to afford coupling partner **6**.



3. Stereocontrolled *C*-glycoside construction

Heck coupling of triflate **12** with glycal **7** (prepared conveniently from thymidine in three steps[14]), under conditions slightly modified from our previous work,[5] followed by in situ fluoride-promoted desilylation, afforded the aryl β-*C*-glycoside **15** in 78% yield for the two steps (1.2 mmol scale). The use of the phase-transfer compound tetrabutylammonium bromide in Heck couplings under anhydrous conditions significantly improves reaction yields.[19] However, under these reaction conditions, the predominate product was ketone **15**, accompanied by only a small amount of the expected silyl enol ether; we treated the crude reaction mixture with HF·pyridine prior to purification. (In the coupling reaction with triflate **6**, this added step was not necessary.)



The amount of Ph_3P significantly affected the reaction yield: 2 equiv. relative to palladium resulted in a slow coupling accompanied by noticeable amounts of the C4′ epimerized compound; with no Ph_3P the reaction proceeded much more rapidly on a small scale, but these conditions were not amenable to scale-up, as yields were lowered because of catalyst instability; in the presence of one equivalent of Ph_3P, the reaction

proceeded at a rate not noticeably slower than that observed in the absence of phosphine, and only trace amounts ($\leq 5\%$) of the C4′ epimerized product were evident. These results suggest that the Heck coupling is proceeding via a non-polar pathway.[20] Hydroxyl-directed reduction of the ketone of **15** using tetramethylammonium triacetoxyborohydride[21] in the presence of acetic acid provided the diol **2** in acceptable yields. Use of sodium triacetoxyborohydride proved less effective due to the insolubility of ketone **15** in acetonitrile.

The synthesis of the regioisomeric 1-anthracenyl β-*C*-glycoside **3** proceeded uneventfully from **6** and **7** using essentially identical reaction conditions. It this case, a separate fluoride-promoted desilylation was unnecessary after the Heck coupling, as the ketone **4** was the sole product of this reaction (86%, 0.64 mmol scale). As it turns out, 2-bromoanthracene (**10**) participates only slightly less effectively than triflate **6** in the Heck coupling (67%, 1.0 mmol scale).

4. Experimental

4.1. 1-Hydroxyanthracene (14)

1-Aminoanthracene (**13**) (1.01 g, 5.23 mmol) and ethanol (9.5 mL) were warmed in a 25 mL flask to effect dissolution. Slow addition of water (19 mL) formed a suspension. After addition of a saturated aqueous $NaHSO_3$ solution (28 mL), the reaction mixture was warmed at reflux for 24 h. While still hot, aqueous KOH (6 M, 25 mL) was added to the clear orange mixture and the reaction was stirred for an additional 2 h. Concentrated aqueous HCl (27.5 mL) was added dropwise until bubbling ceased; the reaction mixture was stirred for 30 min, and was cooled and filtered, affording a yellowish residue that was dissolved in ether (100 mL) and filtered. The filtrate was concentrated to give 1-hydroxyanthracene (**14**) (820.2 mg, 81%) as a yellow–gray solid that was sufficiently pure to be used without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.41 (s, 1H), 8.06 (m, 1H), 8.00 (m, 1H), 7.63 (d, $J=8.6$ Hz, 1H), 7.48 (m, 2H), 7.31 (dd, $J=8.6$, 7.2 Hz, 1H), 6.78 (d, $J=7.1$ Hz, 1H), 5.34 (s, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 154.4, 134.4, 133.3, 132.3, 129.9, 129.2, 127.1, 126.8, 126.8, 126.3, 122.3, 120.6, 107.0, 106.9; HRMS (ES), m/z 194.0713 (calcd for $C_{14}H_{10}O$: 194.0726).

4.2. 1-Hydroxyanthracene trifluoromethanesulfonate (6)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.51 (s, 1H), 8.11 (m, 1H), 8.04 (m, 2H), 7.57 (m, 2H), 7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 132.7, 132.6, 132.5, 129.2, 128.9, 128.3, 127.2, 126.9 (2C), 124.9, 124.0, 120.2, 119.1 (q, $J=320.6$ Hz), 117.0; IR (neat) ν_{max} 1420, 1211, 1139, 1124, 997, 887, 824, 725, 596, 469 cm^{-1}; HRMS (EI), m/z 326.0199 (calcd for $C_{15}H_9O_3SF_3$: 326.0219).

4.3. 1′-Anthracen-1-yl-3′-keto-2′-deoxy-*C*-riboside (4)

Trifluoromethanesulfonate **6** (209.6 mg, 0.642 mmol), $NaHCO_3$ (175.1 mg, 2.08 mmol, 3.24 equiv.), *n*-Bu_4NBr (210 mg, 0.651 mmol, 1.01 equiv.), and 4 Å molecular sieves (285.6 mg) were added to a 10 mL flask and placed under vacuum for 30 min. Glycal **7** was dissolved in dry DMF (3.5 mL) and added to the flask under N_2. The reaction mixture was warmed at 80°C. The $Pd(OAc)_2$ (37.5 mg, 0.167 mmol, 0.26 equiv.), and Ph_3P (42.5 mg, 0.162 mmol, 0.252 equiv.) were added to the reaction mixture. After 2 h at 80°C, the reaction mixture was filtered through Celite (CH_2Cl_2 wash), the filtrate was extracted with water (3×30 mL), and the organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (2.5× 20 cm silica, 35% EtOAc/hexanes) to afford ketoalcohol **4** (161.8 mg, 86%) as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.50 (s, 1H), 8.03 (m, 3H), 7.75 (d, $J=6.9$ Hz, 1H), 7.51 (m, 3H), 6.08 (dd, $J=11.1$, 5.8 Hz, 1H), 4.28 (t, $J=3.5$ Hz, 1H), 4.09 (m, 2H), 3.22 (dd, $J=18.1$, 5.8 Hz, 1H), 2.79 (dd, $J=18.1$, 11.1 Hz, 1H), 2.06 (dd, $J=7.0$, 6.1, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.0, 135.4, 132.1, 132.0, 131.6, 129.5, 129.0, 128.6, 128.1, 127.6, 126.1, 126.0, 124.9, 122.5, 122.1, 82.5, 75.6, 61.8, 44.9; IR (neat) ν_{max} 3448, 3048, 2919, 2866, 1756, 1452, 1387, 1308, 1164, 1105, 1046, 876, 732, 691, 468 cm^{-1}; HRMS (ES), m/z 315.0997 (calcd for $C_{19}H_{16}O_3$+Na: 315.0992).

4.4. 1′-Anthracen-1-yl-2′-deoxy-*C*-riboside (3)

Ketoalcohol **4** (32.4 mg, 0.11 mmol) and glacial acetic acid (20 μL, 0.373 mmol, 3.37 equiv.) were warmed in THF (2 mL) to effect dissolution. $Me_4NBH(OAc)_3$ (206.1 mg, 0.783 mmol, 7.1 equiv.) was added to this mixture at 24°C. After stirring for 3 h at this temperature, saturated aqueous NH_4OH (0.8 mL) was added followed by an aqueous sodium potassium tartrate solution (1M, 3 mL). After stirring for 40 min, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (1×12 cm silica, EtOAc) to afford the diol **3** (27.9 mg, 86%) as a light-yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.47 (s, 1H), 8.04 (m, 1H), 8.00 (m, 1H), 7.97 (d, $J=8.4$ Hz, 1H), 7.65 (d, $J=7.0$ Hz, 1H), 7.50 (m, 2H), 7.46 (dd, $J=8.4$, 7.0 Hz, 1H), 6.06 (dd, $J=10.0$, 5.8 Hz, 1H), 4.58 (m, 1H), 4.22 (q, $J=4.0$, 1H), 3.97 (m, 1H), 3.89 (m, 1H), 2.66 (ddd, $J=13.2$, 5.8, 2.3 Hz, 1H), 2.26 (ddd, $J=13.1$, 9.8, 6.5 Hz, 1H), 1.98 (br d, 1H), 1.90 (br t, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 140.0, 133.4, 132.9, 132.6, 130.5, 129.8, 129.1, 129.0, 128.1, 126.8, 126.7, 126.3, 123.6, 122.9, 89.1, 78.2, 74.4, 64.3, 44.4; IR (neat) ν_{max} 3376, 2919, 2853, 1455, 1375, 1302, 1260, 1091, 1062, 871, 732, 467 cm^{-1}; HRMS (ES), m/z 317.1141 (calcd for $C_{19}H_{18}O_3$+Na: 317.1148).

4.5. 2-Bromoanthraquinone (9)

Cupric bromide (55.5 g, 0.249 mol, 2 equiv.) was dissolved in CH_3CN (300 mL) in a 2 L flask. *tert*-Butyl

nitrite (30 mL) was added to the reaction mixture with stirring. 2-Aminoanthraquinone (**8**) (24.03 g, 124.4 mmol) was dissolved in THF (400 mL) and placed in an addition funnel affixed to the reaction flask. The anthraquinone solution was added at 25°C over a 20 min period, and the reaction mixture was stirred for 20 h. The reaction mixture was concentrated and the solid residue was triturated with water. This slurry was filtered and the solid was washed with H_2O. The solid was washed with CH_2Cl_2 through the filter paper and the organic filtrate was concentrated. This trituration process was repeated. The organic filtrate was extracted with H_2O and the organic layer was concentrated. Although this procedure provided reasonably pure material (26.9 g, 75%), it was further purified from polar material by flash chromatography (8×20 cm silica, 15% EtOAc/hexanes) to afford 2-bromoanthraquinone **9** (24.21g, 68%) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, $J=2.0$ Hz, 1H), 8.33 (m, 2H), 8.19 (d, $J=8.3$ Hz, 1H), 7.94 (dd, $J=8.3$, 2.0 Hz, 1H), 7.84 (m, 2H); HRMS (EI) m/z 285.9615 (calcd for $C_{14}H_7O_2Br$: 285.9624).

4.6. 2-Bromoanthracene (10)

2-Bromoanthraquinone (**9**) (24.21 g, 84.3 mmol) and isopropanol (300 mL) were added to a 500 mL flask at 25°C and stirred to create a suspension. The reaction mixture was treated with $NaBH_4$ (13.64 g, 360 mmol, 4.3 equiv.) and was stirred, as the yellow suspension turned brown and then green. After 15 h at 25°C, the suspension was poured onto an ice-water mixture and filtered to give a light yellow brown solid that was used without purification. The solid was placed in a 1 L flask, treated with aqueous HCl (3 M, 500 mL), and heated at 75°C for 8 h. The suspension was cooled and filtered (H_2O wash) to give a brownish-yellow solid that was used without further purification. The solid was placed in a 500 mL flask with and dissolved in isopropanol (300 mL). The reaction mixture was treated with $NaBH_4$ (19.05 g, 503.6 mmol, 6 equiv.) at 25°C and the mixture was warmed at reflux for 20 h. Aqueous 3 M HCl was added until bubbling ceased and the mixture was filtered to provide an off-yellow residue that was washed through the filter paper with CH_2Cl_2. The filtrate was concentrated to provide a yellowish solid that was purified by flash chromatography (8×15 cm silica, 10% CH_2Cl_2/hexane) to afford 2-bromoanthracene (**10**) (11.7 g, 54%) as a yellow solid that was contaminated with 20 mol% anthracene. Spectral data for **10**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.34 (s, 1H), 8.19 (d, $J=1.0$, 1H), 8.01 (m, 2H), 7.89 (d, $J=9.2$ Hz, 1H), 7.51 (m, 3H); HRMS (EI) m/z 255.9861 (calcd for $C_{14}H_9Br$ 255.9882).

4.7. 2-Hydroxyanthracene (11)

2-Bromoanthracene (**10**) (6.12 g, 23.8 mmol) was dissolved in dry THF (200 mL) under N_2. A solution of *n*-BuLi (18.0 mL, 2.27 M in hexane, 40.9 mmol, 1.7 equiv.) was added to the reaction mixture at −78°C to afford a dark red solution upon warming to −15°C. The reaction mixture was cooled to −78°C and tri-*n*-butyl borate (20 mL, 74.1 mmol, 3.11 equiv.) was added. As the mixture warmed to 0°C, it turned a light yellow color. At 0°C, a saturated aqueous $(NH_4)_2SO_4$ solution (50 mL) was added and the mixture was stirred for 15 min. The organic layer was separated and concentrated to provide a yellow residue, which was dissolved in methanol (200 mL) and water (50 mL). Hydrogen peroxide (20 mL, 30% aqueous solution) was added to this mixture at 0°C with stirring. After 3 h, a saturated aqueous $(NH_4)_2SO_4$ solution (100 mL) was added and the mixture was extracted with CH_2Cl_2. The organic layer was concentrated and the residue was purified by flash chromatography (4×15 cm silica, 15% CH_2Cl_2/hexanes then 25% EtOAc/hexanes) to afford 2-hydroxyanthracene (**11**) (2.364 g, 51%) as a yellow solid: ^{1}H NMR (400 MHz, acetone-d_6) δ 8.77 (br s, 1H), 8.43 (s, 1H), 8.25 (s, 1H), 7.97 (m, 3H), 7.43 (dt, $J=8.2$, 1.4 Hz, 1H), 7.38 (dt, $J=8.2$, 1.2 Hz, 1H), 7.31 (d, $J=2.2$ Hz, 1H), 7.21 (dd, $J=9.1$, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 155.6, 134.1, 133.1, 130.9, 130.8, 129.0, 128.8, 128.2, 127.0, 126.2, 124.9, 124.0, 121.0, 107.6.

4.8. 2-Hydroxyanthracene trifluoromethanesulfonate (12)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.45 (s, 1H), 8.08 (d, $J=9.3$ Hz, 1H), 8.03 (m, 2H), 7.91 (d, $J=2.3$ Hz, 1H), 7.55 (m, 2H), 7.36 (dd, $J=9.3$, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 132.6, 132.5, 131.5, 130.8, 130.2, 128.5, 128.2, 127.2, 127.1, 126.7, 126.5, 119.7, 119.3, 119.1 (q, $J=320.8$ Hz); IR (KBr) ν_{max} 1620, 1437, 1420, 1248, 1208, 1126, 956, 897, 808, 744, 597, 503, 468 cm^{-1}; HRMS (EI), m/z 326.0199 (calcd for $C_{15}H_9O_3SF_3$: 326.0219).

4.8.1. 1′-Anthracen-2-yl-3′-keto-2′-deoxy-*C*-riboside (15). Triflate **12** (385.9 mg, 1.18 mmol), $NaHCO_3$ (310.3 mg, 3.69 mmol, 3.12 equiv.), *n*-Bu_4NBr (394.6 mg, 1.224 mmol, 1.04 equiv.), 3 Å molecular sieves (474.8 mg), $Pd(OAc)_2$ (66.8 mg, 0.298 mmol, 0.252 equiv.) and Ph_3P (77.4 mg, 0.295 mmol, 0.250 equiv.) were added to a 4 dram vial and placed under vacuum for 1 h. A solution of glycal **7** (806.1 mg, 3.50 mmol, 2.96 equiv.) in dry DMF (4 mL) and added to the vial under N_2, and the vial was warmed at 60°C. After 40 min, additional $Pd(OAc)_2$ was added (14.4 mg, 0.064 mmol, 0.054 equiv.). After 2 h at 60°C, the reaction mixture was filtered through Celite (CH_2Cl_2 wash), the filtrate was extracted with water (3×30 mL) and the organic layer was dried (Na_2SO_4) and concentrated. The residue was dissolved in dry THF (40 mL) and was treated with HF/pyridine (1.5 mL) for 6 h at 27°C. The reaction mixture was concentrated and the residue was purified by flash chromatography (4×12 cm silica, 35% EtOAc/CH_2Cl_2) to afford ketoalcohol **15** (268.6 mg, 78%) as a light yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 2 H), 8.08 (d, $J=8.9$ Hz, 1H), 8.05 (br s, 1H), 8.03 (m, 2H), 7.54 (dd, $J=8.8$, 1.7 Hz, 1H), 7.50 (m, 2H), 5.45 (dd, $J=11.0$, 5.8 Hz, 1H), 4.15 (t, $J=3.4$ Hz, 1H), 4.04 (m, 2H), 3.01 (dd, $J=18.1$, 5.9 Hz, 1H), 2.73 (dd, $J=18.1$, 10.9 Hz, 1H), 2.08 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.9, 136.4, 132.3, 132.2, 131.6, 131.3,

129.6, 128.4, 128.4, 126.8, 126.5, 125.9 (2C), 125.8, 123.4, 82.5, 78.2, 61.9, 45.3; IR (KBr) ν_{max} 3495, 2919, 1752, 1168, 1110, 1066, 1034, 1001, 909, 894, 754, 471 cm^{-1}; HRMS (ES), m/z 315.0995 (calcd for $C_{19}H_{16}O_3$+Na: 315.0992).

4.9. 1′-Anthracen-2-yl-2′-deoxy-*C*-riboside (2)

Following the procedure for the synthesis of **3**, ketoalcohol **15** (265 mg, 0.906 mmol), glacial acetic acid (200 μL, 3.73 mmol, 4.11 equiv.) and $Me_4NBH(OAc)_3$ (1.31 g, 4.98 mmol, 5.49 equiv.) afforded **3** (197 mg, 74%) as a light-yellow solid: ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.02 (m, 3H), 7.99 (d, $J=10.4$ Hz, 1H), 7.48 (m, 2H), 7.44 (dd, $J=8.85$, 1.35 Hz, 1H), 5.40 (dd, $J=10.2$, 5.7 Hz, 1H), 4.54 (m, 1H), 4.12 (q, $J=4.0$ Hz, 1H), 3.91 (m, 1H), 3.84 (m, 1H), 2.39 (ddd, $J=13.4$, 5.8, 1.9 Hz, 1H), 2.22 (ddd, $J=13.4$, 10.2, 6.4 Hz, 1H), 1.94 (br t, 1H), 1.88 (br d, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 140.9, 133.0, 132.7, 132.6, 132.4, 129.1, 129.1, 129.0, 127.0, 126.9, 126.4, 126.2, 125.5, 125.2, 89.4, 81.0, 74.3, 64.2, 44.9; IR (KBr) ν_{max} 3366, 2925, 1738, 1673, 1459, 1436, 1309, 1085, 1044, 894, 741, 474 cm^{-1}; HRMS (ES), m/z 317.1169 (calcd for $C_{19}H_{18}O_3$+Na: 317.1148).

Acknowledgements

This work was supported by a grant from the National Institutes of Health (R01 GM61292).

References

1. Murphy, C. J. Photophysical Probes of DNA Sequence-Directed Structure and Dynamics. *Adv. Photochem.* **2001**, *26*, 145–217.
2. (a) Pecourt, J.-M. L.; Peon, J.; Kohler, B. *J. Am. Chem. Soc.* **2000**, *122*, 9348; (b) Pecourt, J.-M. L.; Peon, J.; Kohler, B. *J. Am. Chem. Soc.* **2001**, *123*, 10370.
3. Barbara, P. F.; Jarzeba, W. *Adv. Chem. Phys.* **1990**, *15*, 1.
4. Maroncelli, M. *J. Mol. Liq.* **1993**, *57*, 1.
5. Coleman, R. S.; Madaras, M. L. *J. Org. Chem.* **1998**, *63*, 5700.
6. Eritja, R.; Walker, P. A.; Randall, S. K.; Goodman, M. F.; Kaplan, B. E. *Nucleosides Nucleotides* **1987**, *6*, 803.
7. (a) Moog, R. S.; Davis, S. G.; Ostrowski, S. G.; Wilson, G. L. *Chem. Phys. Lett.* **1999**, *299*, 265; (b) Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 17311.
8. Brauns, E. B.; Madaras, M. L.; Coleman, R. S.; Murphy, C. J.; Berg, M. A. *J. Am. Chem. Soc.* **1999**, *121*, 11644.
9. Brauns, E. B.; Madaras, M. L.; Coleman, R. S.; Murphy, C. J.; Berg, M. A. *Phys. Rev. Lett.* **2002**, *88*, 158101.
10. The 1-anthracenyl 2′-deoxy-*C*-riboside stereoisomers are described in a patent by Kool (CAN 134:326710), but the coupling of anthracene to the deoxyribose was poorly stereoselective and it relied on the use of stoichiometric cadmium followed by an acid catalyzed anomerization. There are no experimental details in the patent.
11. (a) Morales, R. G. E. *J. Phys. Chem.* **1982**, *86*, 2550; (b) Ghoneim, N.; Suppan, P. *Spectrochim. Acta* **1995**, *51A*, 1043; (c) Renge, I. *J. Photochem. Photobiol. A: Chem.* **1992**, *69*, 135. For time-resolved measurements, see: (d) Zhang, Y.; Berg, M. A. *J. Chem. Phys.* **2001**, *115*, 4231; (e) Zhang, Y.; Jiang, J.; Berg, M. A. *J. Chem. Phys.*, submitted for publication.
12. (a) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, 1971; (b) Lambert, W. R.; Felker, P. M.; Syage, J. A.; Zewail, A. *J. Chem. Phys.* **1984**, *81*, 2195.
13. (a) Cabri, W.; Candiani, I.; DeBernardinis, S.; Francalanci, F.; Penco, S. *J. Org. Chem.* **1991**, *56*, 5796; (b) Cabri, W.; Candiani, I.; Bedeschi, A. *J. Org. Chem.* **1990**, *55*, 3654; (c) Cabri, W.; Candiani, I.; Bedeschi, A. *J. Org. Chem.* **1992**, *57*, 3558; (d) Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2.
14. (a) Cameron, M. A.; Cush, S. B.; Hammer, R. P. *J. Org. Chem.* **1997**, *62*, 9065; (b) Larson, E.; Jorgensen, P. T.; Sofan, M. A.; Pederson, E. B. *Synthesis* **1994**, 1037–1038.
15. (a) Weidhaup, K.; Kesselaar, F. H.; Huisman, H. O. *Tetrahedron* **1968**, *24*, 779; (b) Sammes, P. G. *J. Chem. Soc., Chem. Commun.* **1979**, 33; (c) Sarngadhuran, M. G.; Seshadri, T. R. *Indian J. Chem.* **1966**, *4*, 503; (d) Brisson, C.; Brassard, P. *J. Org. Chem.* **1981**, *46*, 1810; (e) Werntz, J. H. *J. Am. Chem. Soc.* **1935**, *57*, 204; (f) Nicoletti, T. M.; Raston, C. L.; Sargent, M. V. *J. Chem. Soc., Perkin Trans. 1* **1990**, 133; (g) Iwao, M.; Kuraishi, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 4051; (h) Sartor, G.; Bigi, F.; Tao, X.; Porta, C.; Maggi, R.; Predieri, G.; Lanfranchi, M.; Pellinghelli, M. A. *J. Org. Chem.* **1995**, *60*, 6588; (i) Morley, J. A.; Woolsey, N. F. *J. Org. Chem.* **1992**, *57*, 6487; (j) Ihmels, H. *Eur. J. Org. Chem.* **1999**, 1595; (k) Netka, J.; Crump, S. L.; Rickborn, B. *J. Org. Chem.* **1986**, *51*, 1189; (l) Fitzgerald, J. J.; Drysdale, N. E.; Olofson, R. A. *J. Org. Chem.* **1992**, *57*, 7122.
16. Doyle, M. P.; Siegfried, B.; Dellaria, J. F. *J. Org. Chem.* **1977**, *42*, 2426.
17. Klanderman, B. H.; Criswell, T. R. *J. Org. Chem.* **1974**, *39*, 770.
18. von Fierz-David, H. E.; Blangey, L.; Streif, H. *Helv. Chim. Acta* **1946**, *29*, 1718.
19. Tuyet, J. *Tetrahedron* **1996**, *52*, 10113.
20. Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.
21. Evans, D. A.; Chapman, K. T.; Carreira, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 3560.