Pergamon

Tetrahedron Letters 42 (2001) 3057–3060

TETRAHEDRON LETTERS

Synthesis of potential molecular electronic devices containing pyridine units

Stephanie H. Chanteau and James M. Tour*

Department of Chemistry and Center for Nanoscale Science and Technology, Rice University, 6100 Main Street, Houston, TX 77005, USA

Received 16 February 2001; revised 1 March 2001; accepted 6 March 2001

Abstract—Conjugated linear molecules containing pyridyl groups as 'alligator clips' have been synthesized as potential molecular electronic devices using palladium-catalyzed couplings. © 2001 Published by Elsevier Science Ltd.

The use of organic molecules, such as conjugated aromatic oligomers, as single molecule electronic conductors has attracted considerable attention due to their exciting potential in the field of molecular electronics.[1] Recent studies have shown that oligo(phenylene ethynylene)s containing nitro groups can be used as electronic switching and memory devices.[2] Most previous work featured benzenethiolate groups as 'alligator clips', units that link to a metal surface.[3] We now describe a general procedure for the synthesis of molecular devices containing pyridine 'alligator clips'.[4]

Fig. 1 shows the two groups of potential molecular devices that have been synthesized. The first group has a nitro functionality on the internal phenyl ring, which was designed to retain electrons so that the molecule could work as a memory element.[2]

The second group has a nitro and an amino group, which have been shown to work similarly albeit at lower temperature.

The potential molecular devices **2** and **4** were envisioned to have two pyridyl terminal groups so that they could serve as cross-linkers for gold connections.

Scheme 1 outlines the synthesis of **2** from 2,5-dibromonitrobenzene. Compound **1**[5] was easily prepared via Sonogashira[6] coupling of 4-iodopyridine[7] and trimethylsilylacetylene (99%). Potassium carbonate is

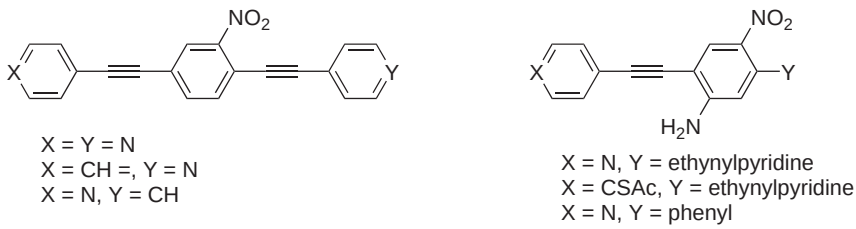
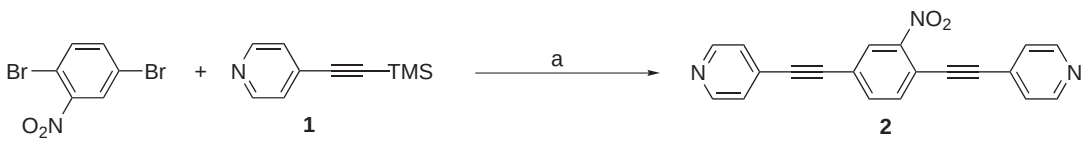


Figure 1. Potential molecular devices containing pyridyl groups as 'alligator clips'.



Scheme 1. (a) K_2CO_3, MeOH, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF, 64°C, 20 h, 24%.

* Corresponding author. E-mail: tour@rice.edu

0040-4039/01/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0040-4039(01)00394-X

used as a base for the in situ removal of the TMS protecting group and for the coupling,[8] as the free alkyne decomposes after a few hours. Attempts to perform the reaction at room temperature gave mostly the bis(ethynylpyridine) and coupling at one site of the aryl dibromide.

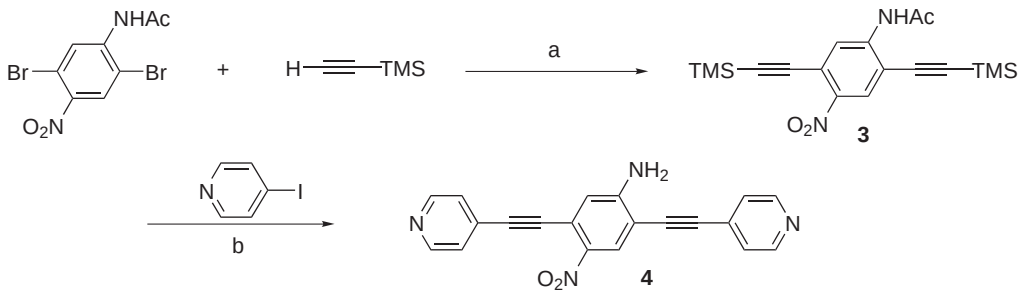
Compound **4** resembles **2**, but has a nitroaniline core instead of a nitro core. Unlike the potential molecular device **2**, the synthesis of **4** (Scheme 2) commenced with the coupling of 2,5-dibromo-4-nitroacetanilide[9] with trimethylsilylacetylene to give **3**, which was then coupled with 4-iodopyridine in low yield. The low yield of the coupling reactions could be due to the cyclization between the nitro and the alkyne unit, a process reported by Rosen et al.[10]

The synthesis of **8** is shown in Scheme 3. Compound **8** has a protected benzenethiol terminal group, which can bind to a gold surface. The other end of the molecule has a pyridyl group, which could possibly serve as a better top-layer linker than the phenyl group. Compound **8** was synthesized by coupling the 2,5-dibromo-4-nitroacetanilide with **1** in a moderate yield to afford compound **5**. Compound **5** was then coupled with trimethylsilylacetylene to afford **6** in 49% yield, which was deprotected with potassium carbonate to give **7**. The last step of this synthesis was the coupling with 4-thioacetyliodobenzene,[11] which afforded the potential device **8** in good yield (75%).

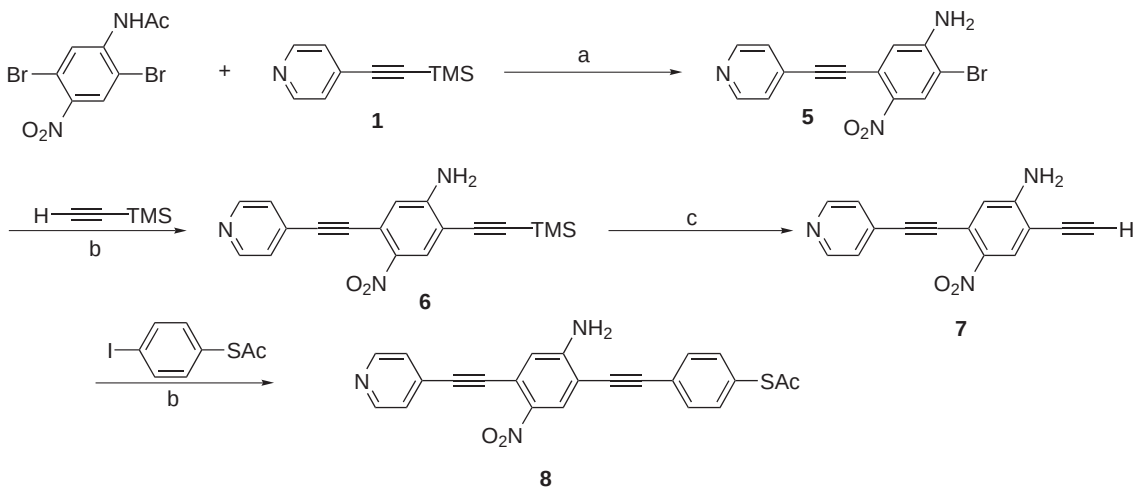
Compounds **10** and **12** were synthesized to study the importance of the position of the nitro group relative to the 'alligator clip' during the self-assembly. Compound **10**, which has the nitro group oriented toward the pyridyl group (Scheme 4), was synthesized by first coupling **1** with 2,5-dibromonitrobenzene, with in situ removal of the TMS group to give **9** in good yield.[12] Coupling of **9** with phenylacetylene afforded **10**.

The synthesis of **12** (Scheme 5), which has the nitro group pointing away from the pyridyl group, resembles the approach used for **10** except that the steps are reversed. In this case, the phenylacetylene was first coupled to 2,5-dibromonitrobenzene to give **11** in a moderate yield. Compound **1** was then coupled to **11** to afford **12** in good yield.

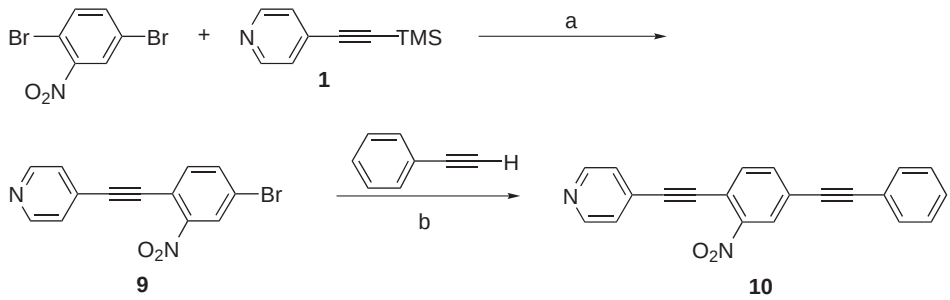
In order to conduct electrons with minimal inhibition, these organic oligomers preferably have all their phenyl rings in the same plane.[1] If the terminal phenylethynyl group is replaced by a phenyl group, the molecule becomes slightly twisted. To study the effect of this rotational barrier, **14** was synthesized. The Suzuki coupling[13] of 2,5-dibromo-4-nitroacetanilide with phenyl boronic acid was used to synthesize compound



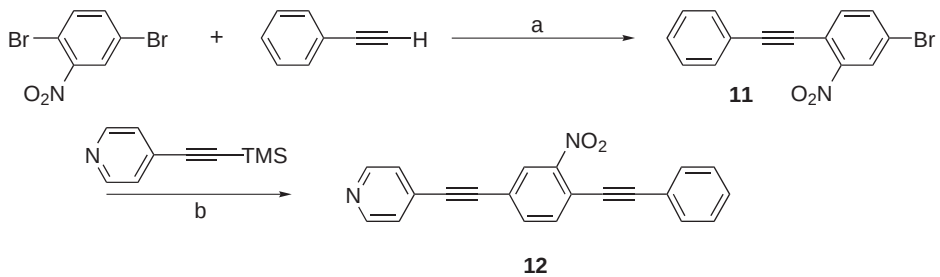
Scheme 2. (a) Et_3N, $Pd(dba)_2$, PPh_3, CuI, THF, 60°C, 48 h, 47%. (b) K_2CO_3, MeOH, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF, 60°C, 50 h, 16%.



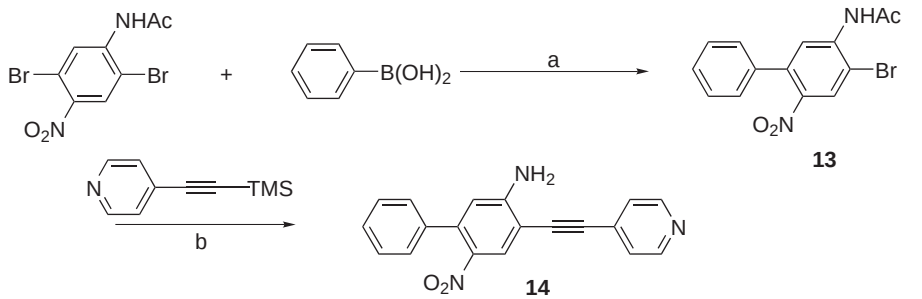
Scheme 3. (a) K_2CO_3, MeOH, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF, rt, 24 h, 39%. (b) Et_3N, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF, 60°C. (c) K_2CO_3, MeOH, CH_2Cl_2, rt, 2 h, 88%.



Scheme 4. (a) K_2CO_3, MeOH, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF, rt, 2 days, 71%. (b) Et_3N, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF, 56°C, 36 h, 69%.



Scheme 5. (a) Et_3N, $Pd(dba)_2$, PPh_3, CuI, THF, rt, 48 h, 47%. (b) K_2CO_3, MeOH, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF, 64°C, 18 h, 79%.



Scheme 6. (a) $Pd(dba)_2$, PPh_3, Cs_2CO_3, toluene, 67°C, 3 days, 51%. (b) K_2CO_3, MeOH, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF, 70°C, 3 days, 79%.

13 (Scheme 6), which was then coupled to 4-(trimethylsilylethynyl)pyridine (**1**) to afford **14**.

The structures of compounds **2**, **4**, **8**, **10**, **12** and **14** were confirmed by IR, ^1H NMR, ^{13}C NMR and MS.[14]

In conclusion, the synthesis of conjugated aromatic molecules containing pyridine units for molecular electronics was accomplished using palladium-catalyzed couplings. The testing of these potential molecular devices is currently underway.

Acknowledgements

This work was supported by grants from the Defense Advanced Research Project Agency, the Office of Naval Research and the Army Research Office. We thank Dr. I. Chester of FAR Laboratories for trimethylsilylacetylene.

References

1. (a) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791; (b) Tour, J. M.; Kozaki, M.; Seminario, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 8486; (c) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, II, L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.
2. (a) Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, *286*, 1550; (b) Chen, J.; Wang, W.; Reed, M. A.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *Appl. Phys. Lett.* **2000**, *77*, 1224; (c) Reed, M. A.; Chen, J.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *Appl. Phys. Lett.*, in press.
3. (a) Tour, J. M.; Jones, II, L.; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529; (b) Vondrak, T.; Cramer, C. J.; Zhu, X.-Y. *J. Phys. Chem. B* **1999**, *103*, 8915.
4. (a) Sun, S.-S.; Lees, A. J. *J. Am. Chem. Soc.* **2000**, *122*, 8956; (b) Sun, S.-S.; Lees, A. J. *Inorg. Chem.* **1999**, *38*, 4181.

5. (a) Ziessel, R.; Suffert, J.; Youinou, M.-T. *J. Org. Chem.* **1996**, *61*, 6535; (b) Champness, N. R.; Khlobystov, A. N.; Majuga, A. G.; Schröder, M.; Zyk, N. V. *Tetrahedron Lett.* **1999**, *40*, 5413; (c) Whiteford, J. A.; Lu, C. V.; Stang, P. J. *J. Am. Chem. Soc.* **1997**, *119*, 2524; (d) Ziessel, R.; Suffert, J. *Tetrahedron Lett* **1991**, *32*, 757.
6. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467.
7. Coudret, C. *Synth. Commun.* **1996**, *26* (19), 3543.
8. **Typical procedure for the in-situ removal of the TMS protecting group and the Sonogashira coupling**: To a solution of the aryl bromide (1.0 mmol), K_2CO_3 (5.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.05 mmol), copper(I) iodide (0.05 mmol) and triphenylphosphine (0.20 mmol) in THF (2 mL) under nitrogen were added via a cannula **1** (1.20 mmol) in THF (2 mL) and MeOH (1 mL). The mixture was heated at 60°C for 12 h–2 days. The solvent was removed by rotary evaporation and the brown residue was diluted with water and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel) afforded the title compound.
9. (a) Tour, J. M.; Lamba, J. J. S. *J. Am. Chem. Soc.* **1993**, *115*, 4935; (b) Lamba, J. J. S.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11723; (c) Moroni, M.; Le Moigne, J.; Pham, T. A.; Bigot, J.-Y. *Macromolecules* **1997**, *30*, 1964.
10. Rosen, G. M.; Tsai, P.; Barth, E. D.; Dorey, G.; Casara, P.; Spedding, M.; Halpern, H. J. *J. Org. Chem.* **2000**, *65*, 4460.
11. Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376.
12. Huang, S.; Tour, J. M. *Tetrahedron Lett.* **1999**, *40*, 3347.
13. (a) Alonso, D. A.; Nájera, C.; Pacheco, M. C. *Org. Lett.* **2000**, *13*, 1823; (b) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
14. Selected spectral data. **2**: IR (KBr) 3414.0, 3036.7, 1616.0, 1589.4, 1538.1, 1519.9, 1407.9, 1345.7, 1271.1, 1214.1, 828.3 cm^{-1}. ^1H NMR (400 MHz, DMSO-*d*) δ 8.69 (br s, 4H), 8.44 (d, $J=1.4$ Hz, 1H), 8.04 (1/2 ABqd, $J=8.0$, 1.4 Hz, 1H), 7.99 (1/2 ABq, $J=8.0$ Hz, 1H), 7.60 (d, $J=5.8$ Hz, 2H), 7.57 (d, $J=5.8$ Hz, 2H). ^{13}C NMR (100 MHz, DMSO-*d*) δ 150.21, 150.13, 149.42, 136.27, 135.36, 129.16, 129.11, 127.96, 125.50, 125.39, 123.25, 116.55, 94.98, 90.63, 90.59, 88.13. HRMS calcd for $C_{20}H_{11}N_3O_2$: 325.0851, found: 325.0847. **4**: IR (KBr) 3730.2, 3438.6, 2204.8, 1592.4, 1541.1, 1409.8, 1308.5, 1249.9, 818.8 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, $J=4.4$, 1.7 Hz, 2H), 8.65 (dd, $J=4.5$, 1.7 Hz, 2H), 8.34 (s, 1H), 7.44 (dd, $J=4.5$, 1.7 Hz, 2H), 7.40 (dd, $J=4,4$, 1.6 Hz, 2H), 6.99 (s, 1H), 5.03 (br s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.26, 150.03, 149.90, 139.56, 130.71, 130.52, 130.00, 125.65, 125.33, 120.33, 118.52, 106.57, 94.67, 94.19, 89.55, 87.27. HRMS calcd for $C_{20}H_{12}N_4O_2$: 340.0960, found: 340.0958. **8**: IR (KBr) 3438.2, 3195.9, 2922.4, 1695.4, 1627.7, 1596.5, 1545.1, 1514.8, 1477.2, 1402.8, 1316.4, 1249.9 cm^{-1}. ^1H NMR (400 MHz, DMSO-*d*) δ 8.68 (br d, $J=4.0$ Hz, 2H), 8.23 (s, 1H), 7.79 (d, $J=8.1$ Hz, 2H), 7.54 (d, $J=5.0$ Hz, 2H), 7.49 (d, $J=8.0$ Hz, 2H), 7.13 (br s, 2H), 7.06 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d*) δ 192.98, 153.79, 150.13, 136.28, 134.31, 132.32, 130.69, 129.67, 128.66, 125.34, 123.05, 118.70, 118.26, 105.43, 95.72, 92.51, 90.12, 85.54, 30.32. HRMS calcd for $C_{23}H_{15}N_3O_3S$: 413.0834, found: 413.0940. **10**: IR (KBr) 3445.3, 3046.3, 2203.5, 1548.5, 1529.1, 1399.9, 1341.6 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (br d, $J=4.9$ Hz, 2H), 8.27 (d, $J=1.5$ Hz, 1H), 7.76 (1/2 ABqd, $J=8.0$, 1.6 Hz, 1H), 7.72 (1/2 ABqd, $J=8.0$, 0.5 Hz, 1H), 7.56 (m, 2H), 7.45 (dd, $J=5.9$, 1.7 Hz, 2H), 7.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.58, 135.39, 134.65, 131.81, 129.34, 128.54, 127.67, 125.32, 121.85, 116.66, 95.30, 94.30, 88.52, 86.63. HRMS calcd for $C_{21}H_{12}N_2O_2$: 324.0899, found: 324.0895. **12**: IR (KBr) 3442.3, 3053.0, 2209.4, 1631.3, 1584.8, 1524.7, 1404.3, 1344.7, 1269.0, 826.4, 755.2, 686.6 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, $J=4.4$, 1.6 Hz, 2H), 8.27 (br s, 1H), 7.74 (m, 2H), 7.63 (d, $J=1.8$ Hz, 1H), 7.60 (m, 1H), 7.42 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.99, 135.41, 134.65, 132.14, 130.19, 129.61, 128.54, 127.95, 125.50, 122.68, 122.06, 119.15, 99.67, 90.83, 90.27, 84.62. HRMS calcd for $C_{21}H_{12}N_2O_2$: 324.0899, found: 324.0897. **14**: IR (KBr) 3410.2, 3323.4, 3212.1, 2215.1, 1627.6, 1592.4, 1548.4, 1511.7, 1410.5, 1331.9 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.64 (br d, $J=4.8$, 2H), 8.16 (s, 1H), 7.39 (m, 5H), 7.27 (m, 2H), 6.62 (s, 1H), 5.03 (br s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.23, 149.82, 140.65, 138.82, 138.19, 130.49, 128.36, 128.06, 127.52, 125.34, 116.41, 104.85, 93.24, 87.89. HRMS calcd for $C_{19}H_{13}N_3O_2$: 315.1008, found: 315.1011.