Naphtho[1,8-*bc*: 5,4-*b*′*c*′]dithiophene: A New Heteroarene Isoelectronic with Pyrene

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The title compound is prepared as a new heteroarene isoelectronic with pyrene, having a stronger electron donating ability than pyrene and isomeric naphtho[1,8-*bc*: 4,5-*b*′*c*′]dithiophene.

Polycyclic heteroarenes have been recently studied in view of their abilities to act as π-electron donors for conductive charge-transfer complexes.[1] In particular, *peri*-condensed heteroarenes isostructural or isoelectronic with pyrene and perylene are of great interest,[2] since these hydrocarbons have been long known as prototypical electron donors.[3] As isoelectronic analogues of pyrene, we recently reported on the syntheses and properties of naphtho[1,8-*bc*: 4,5-*b*′*c*′]dithiophene **1**[4,5] and its 2,5-dimethyl and bis(methylthio) derivatives.[5] Moradpour also reported an independent synthesis of the 2,5-dimethyl derivative.[6] The introduction of the sulfur atoms leads to not only considerable lowering of oxidation potentials but also enhancement of intermolecular interactions. In this regard, isomeric naphtho[1,8-*bc*: 5,4-*b*′*c*′]dithiophene **2** is more interesting because it contains no Kekulé benzene ring in the structure with C_{2h} symmetry in contrast to C_{2v} counterpart **1**. Thus the former is expected to have a much lower oxidation potential than does the latter. A MNDO MO calculation also predicts the elevation of the HOMO level of **2** (−7.982 eV) as compared to **1** (−8.223 eV).[7] Although the initial synthesis of **1** was accomplished *via* [2.2]thiophenophanediene, a similar approach to **2** was unsuccessful.[4] This result suggested lower stability of **2** and has prompted us to study an alternative route. After the elaborate search of some potential approaches, we have developed a successful route to **2** *via* 3,3′-bithienyl derivatives, as described below.

As shown in Scheme 1, the synthesis of **2** was carried out *via* 5,5′-dibromo-2,2′,4,4′-tetramethyl-3,3′-bithienyl **3**, which was prepared in five steps from commercially available 3-methylthiophene according to the reported procedure of Wiklund and Håkansson.[8] Bromination of **3** with excess *N*-bromosuccinimide gave 4,4′-bis(bromomethyl)-2,2′-bis(dibromomethyl)-5,5′-dibromo-3,3′-bithienyl **4** in 83% yield. The subsequent hydrolysis of **4** with dilute sulfuric acid afforded 5,5′-dibromo-4,4′-bis(bromomethyl)-2,2′-diformyl-3,3′-bithienyl **5** in 95% yield, which was then converted into the phosphonate **6** in a quantitative yield by treatment with trimethylphosphite. Intramolecular Wittig–Horner reaction of **6** using sodium methoxide as a base led to the formation of 2,6-dibromonaphtho[1,8-*bc*: 5,4-*b*′*c*′]dithiophene **7** in 22% yield. Its conversion to the parent **2** was achieved in 59% yield by treatment of **7** with *n*-butyllithium followed by water.†

Compound **2** is a yellow crystalline material which, unlike **1**, is very sensitive to air in solution and tends to gradually decompose even in the solid state. The dibromo derivative **7** is slightly more stable. The electronic spectrum of **2** showed three absorption bands at 236.0, 328.4 and 408.4 nm in cyclohexane, the latter two of which are accompanied by fine structure peaks. A comparison of the long-wavelength bands with the corresponding absorptions of **1** (299.2 and 352.8 nm) and pyrene (272.6 and 334.6 nm) indicates significant bathochromic shifts, reflecting a smaller HOMO–LUMO band gap of **2** than those of **1** and pyrene. The electrochemical behaviour of **2** and **7** studied by cyclic voltammetry showed irreversible anode peaks at +0.93 and +1.04 V, respectively, *vs.* Ag/AgCl in benzonitrile. The lower oxidation potential of **2** than those of **1** (+1.01 V) and pyrene (+1.35 V) clearly supports an increasing electron donating ability of **2** as expected.

Although the lability of **2** gave rise to some difficulty in its complexation study, it formed black materials with iodine and with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, which had high electrical conductivities of 0.20 and 0.08 S cm^{-1}, respectively. This suggests that **2** has potential as a component of conductive charge-transfer complexes. Further chemical modifications directed towards the stabilization of **2** are now under way.

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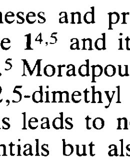
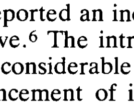
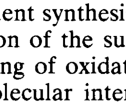


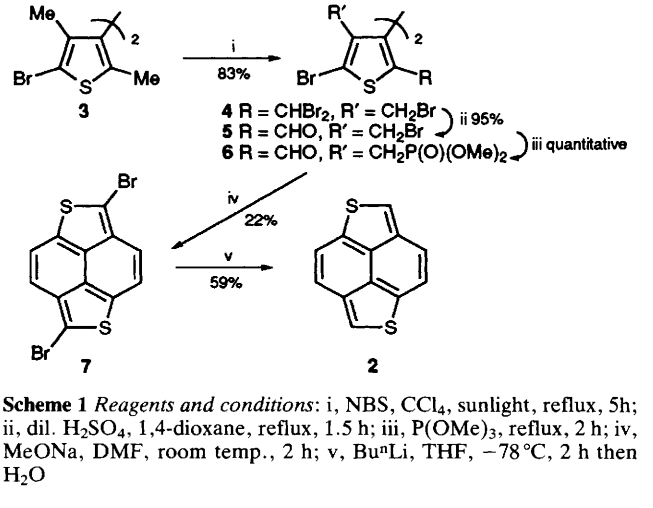
pyrene



1



2



Scheme 1 *Reagents and conditions*: i, NBS, CCl$_4$, sunlight, reflux, 5h; ii, dil. H$_2$SO$_4$, 1,4-dioxane, reflux, 1.5 h; iii, P(OMe)$_3$, reflux, 2 h; iv, MeONa, DMF, room temp., 2 h; v, Bu^{n}Li, THF, −78 °C, 2 h then H$_2$O

Footnote

† *Selected spectral data* for **2**: decomp. 93 °C in a sealed tube; ^{1}H NMR (CDCl$_3$–CS$_2$) δ 7.47 (d, *J* = 9.2 Hz, 2H), 7.61 (s, 2H) and 7.65 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (CDCl$_3$–CS$_2$) δ 116.9, 118.9, 121.6, 129.6, 132.4 and 133.7; MS, *m/z* 213.9911 (M$^+$) (Calc. 213.9918); λ_{max} 236.0 (log ε 4.24), 313.4 (3.85), 328.4 (4.03), 379.6 (4.09), 385.0 (4.13), 396.2 (4.15), 402.0 (4.28) and 408.4 (4.26) nm in cyclohexane. For **7**: decomp. 102 °C in a sealed tube; ^{1}H NMR (CDCl$_3$–CS$_2$) δ 7.34 (d, *J* = 9.3 Hz) and 7.62 (d, *J* = 9.3 Hz); MS, *m/z* 370, 372 and 374 (M$^+$).

References

1 D. J. Sandman and G. P. Ceasar, *Isr. J. Chem.*, 1986, **27**, 293.

2 F. Wudl, R. C. Haddon, E. T. Zellers and F. B. Bramwell, *J. Org. Chem.*, 1979, **44**, 2491; K. Bechgaard, *Mol. Cryst. Liq. Cryst.*, 1985, **125**, 81; K. Nakasuji, *Pure Appl. Chem.*, 1990, **62**, 477; J. B. Christensen, I. Johannsen and K. Bechgaard, *J. Org. Chem.*, 1991, **56**, 7055; T. Otsubo, Y. Kono, N. Hozo, H. Miyamoto, Y. Aso, F. Ogura, T. Tanaka and M. Sawada, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 2033.

3 H. Akamatu, H. Inokuchi and Y. Matsunaga, *Nature* (*London*), 1954, **173**, 168; *Bull. Chem. Soc. Jpn.*, 1956, **29**, 213; J. Kommandeur and F. R. Hall, *J. Chem. Phys.*, 1961, **34**, 129; T. C. Ching, A. H. Reddoch and D. F. Williams, *J. Chem. Phys.*, 1971, **54**, 2051; C. Kröhnke, V. Enkelmann and G. Wegner, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 912; G. Heywang and S. Roth, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 176.

4 K. Watanabe, Y. Aso, T. Otsubo and F. Ogura, *Chem. Lett.*, 1992, 1233.

5 K. Takimiya, F. Yashiki, Y. Aso, T. Otsubo and F. Ogura, *Chem. Lett.*, 1993, 365.

6 A. Moradpour, *J. Chem. Soc., Perkin Trans. 1*, 1993, 7.

7 MO calculations were performed by using the MNDO method (MOPAC Ver. 5.00 (QCPE no. 445), J. J. P. Stewart, *QCPE Bull.* 1989, **9**, 10; T. Hirano, *JCPE Newsletter*, 1989, **1**, 36; Revised as Ver. 5.01 by J. Toyoda for Apple Macintosh).

8 E. Wiklund and Håkansson, *Chem. Scr.*, 1973, **3**, 220.