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LETTERS

Versatile syntheses of functionalised 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives

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Abstract

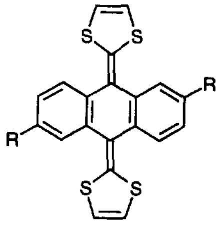
Two new synthetic approaches to functionalised derivatives of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system are reported. A range of new derivatives bearing reactive substituents are described.

Keywords: dithioles; anthracenes; lithiation; electron donors

Bis(1,3-dithiole) electron donors with extended π-conjugation have received considerable attention as tetrathiafulvalene (TTF) analogues in the fields of molecular conductors and materials with interesting optical properties. Representative derivatives include those with vinylogous conjugation between the two dithiole rings,[1] or the incorporation of quinonoid[2] or heteroaromatic[3] spacer units. In this context, the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system **1**[2] is especially interesting. Important features of system **1** are (i) its high electron donor ability, which is characterised by a single, two-electron, redox wave to yield a thermodynamically stable dication at E^{ox} *ca* +0.3 V (*vs* Ag/AgCl) in the cyclic voltammogram; (ii) the unusual saddle-shaped structure of the molecule which is enforced by the boat conformation of the central anthracenediylidene ring, which arises as a consequence of steric crowding of the sulfur atoms and the *peri* hydrogens.[4] Taken together these properties afford a novel redox-active concave cavity.[5]

We now report our work on the synthesis of a new and versatile range of derivatives of **1** which contain a reactive functional group attached to one of the 1,3-dithiole rings. These derivatives are designed to enable system **1** to be exploited as a functionalised building block in the fields of supramolecular and materials chemistry. This is a new direction for studies on system **1**. The known derivatives of **1** are restricted to those with simple alkyl,[2b,4a] thioalkyl[6] or aryl[7] substituents on the dithiole rings, which are not suitable for further functionalisation. Heterocyclic analogues,[8] and a few derivatives with substituents attached to the anthracenediylidene spacer have been reported.[9]

The low solubility of **1** hampered attempts to prepare lithiated derivatives. We, therefore, attempted to monolithiate the more soluble dibutoxy derivative **2**,[10] and subsequently react this species with electrophiles, by analogy with TTF.[11] However, complex mixtures of various di- and multi-lithiated products were always obtained. To circumvent this problem, by ensuring that only mono-lithiation occurred,[12] we synthesised the new trimethyl derivative **5**[13] in 55% yield, by reaction of compound **3**[2b] with the phosphonate anion obtained by deprotonation of reagent **4** using lithium diisopropylamide (LDA) in THF at -78 °C[14] (Scheme 1).



1 R = H
2 R = O-*n*-Bu

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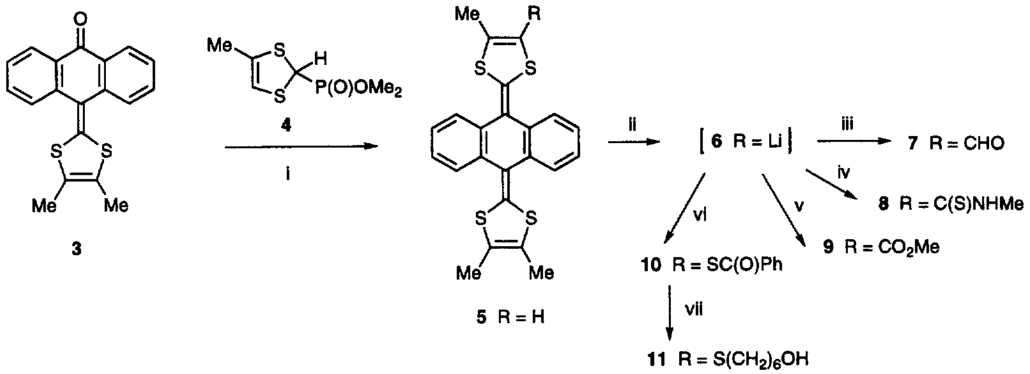
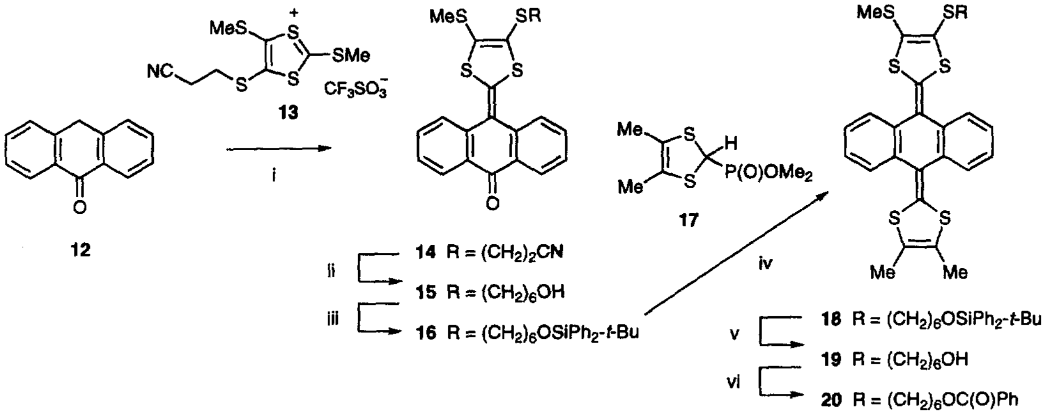
Compound **5** was then deprotonated using LDA in THF at -78 °C; quenching the anion with excess D_2O gave a quantitative yield of the mono-deuterio derivative of **5** (^1H NMR evidence) confirming the very efficient generation of species **6**. The results of trapping species **6** with a selection of electrophiles is shown in Scheme 1. In general, yields of substituted products **7-10** are consistently lower than those for analogous trimethyl-TTF derivatives.[12] When product yields were low, the majority of unreacted compound **5** was recovered.

For example, aldehyde and thioamide derivatives **7** and **8** could be obtained repeatedly in only 13 and 17% yields, respectively, with dimethylformamide being preferable to *N*-methyl-*N*-phenylformamide as the formylating reagent in the synthesis of **7**. A more efficient trapping of species **6** occurred with methylchloroformate, to yield the ester derivative **9** (69% yield). Thioester derivative **10** was also obtained cleanly (50% yield) by addition of elemental sulfur to intermediate **6** to generate the corresponding thiolate species, which reacted *in situ* with benzoyl chloride. Compound **10** was designed to be a versatile shelf-stable precursor of other mono-functionalised derivatives of **5**. This was demonstrated by the facile debenzoylation of **10** (sodium methoxide, room temperature) and trapping in a model reaction with 6-bromohexanol to yield **11** (93% yield).



Scheme 1. Reagents, conditions and yields: (i) LDA, THF, -78°C, compound **4**, 1 h, then compound **3** (55%); (ii) LDA, THF, -78°C; (iii) Me_2NCHO, THF, -78°C (13% from **5**); (iv) MeN=C=S, THF, -78°C (17% from **5**); (v) $ClCO_2Me$, THF, -78°C (69% from **5**); (vi) S_8, THF, -78°C, 3 h, then PhC(O)Cl (50% from **5**); (vii) NaOMe, MeOH, 20°C, 1 h, then $Br(CH_2)_6OH$ (93% from **10**).

An alternative approach to mono-functionalised derivatives of **1** is shown in Scheme 2. 1,3-Dithiolium cation salt **13** was prepared by methylation of the corresponding thione[15] and reacted, without purification, with the anion of anthrone **12** to afford compound **14** (17% yield, based on the thione). The low yield was due to the competing deprotection of the thiolate group of **13** under these basic conditions. Deprotection of **14**, using Becher's conditions,[15,16] followed by *in situ* trapping of the cesium thiolate salt with 6-bromohexanol afforded the alcohol derivative **15** in 89% yield. This was protected as its diphenyl-*t*-butylsilyl ether derivative **16** (90% yield) and then reacted with the anion derived from reagent **17**[12] to afford compound **18** in 69% yield. The reactive alcohol functionality was liberated by desilylation with fluoride ion to afford **19** (79% yield). To establish that compound **19** was suitable for further functionalisation, reaction with benzoyl chloride in the presence of triethylamine gave the benzoyl ester derivative **20** in 50% yield.



Scheme 2. Reagents, conditions and yields: (i) LDA, *i*-PrOH, 20°C, 20 min, then **13**, THF (17%); (ii) CsOH·H_2O, THF, MeOH, 20°C, 1 h, then 6-bromohexanol (89%); (iii) *t*-$BuPh_2SiCl$, imidazole, DMF, 20°C (90%); (iv) **17**, LDA, THF, -78°C, 1 h, then **16** (69%); (v) *n*-Bu_4NF, THF, 20°C (79%); (vi) PhC(O)Cl, NEt_3, CH_2Cl_2 (50%).

In summary, we have developed new approaches for the attachment of reactive functionality to the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system. The availability of derivatives such as **9**, **10** and **19** in 0.5 - 1.0 g batches paves the way for the development of the chemistry of this interesting electron donor molecule.

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13 New compounds gave analytical and spectroscopic data consistent with their structures. Selected data: compound **5**: a yellow solid, mp 288-290 °C; ^{1}H NMR ($CDCl_3$) δ 2.02 (s, 6H), 2.14 (s, 3H), 5.93 (s, 1H), 7.36 (m, 4H), 7.75 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.8, 15.9, 111.0, 120.8, 121.2, 122.1, 125.1, 125.3, 125.7, 129.3, 133.0, 135.1, 135.2, 136.0 ppm.

compound **9**: a yellow solid, 218-220 °C; ^{1}H NMR ($CDCl_3$) δ 1.83 (s, 6H), 2.28 (s, 3H), 3.69 (s, 3H), 7.20 (m, 4H), 7.51 (m, 2H), 7.57 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.4, 15.7, 52.4, 117.2, 121.0, 121.2, 123.7, 125.4, 125.5, 125.7, 125.9, 126.1, 126.4, 129.5, 134.2, 134.8, 135.5, 145.8, 160.9 ppm.

compound **10**: a yellow solid, mp *ca.* 160 °C (dec.); ^{1}H NMR ($CDCl_3$) δ 1.84 (s, 6H), 1.97 (s, 3H), 7.19 (m, 4H), 7.39 (t, 2H *J* 7.5 Hz), 7.53 (m, 5H), 7.86 (d, 2H *J* 7.9Hz); ^{13}C NMR ($CDCl_3$) δ 13.1, 14.9, 108.1, 120.8, 120.9, 121.0, 123.0, 125.1, 125.2, 125.4, 125.5, 125.7, 125.8, 126.0, 126.1, 126.8, 126.9, 131.3, 133.9, 134.2, 134.7, 134.9, 135.3, 135.4, 135.7, 139.3, 187.7 ppm.

compound **19**: a yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.39 (m, 4H), 1.56 (m, 4H), 1.93 (s, 6H), 2.37 (s, 3H), 2.77 (m, 2H), 3.61 (t, 2H *J* 6.5 Hz), 7.28 (m, 4H), 7.52 (m, 2H), 7.66 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.1, 19.1, 25.2, 28.1, 29.6, 32.5, 36.0, 60.4, 62.8, 120.9, 123.8, 124.0, 125.3, 125.7, 126.1, 127.7, 130.2, 133.5, 134.5, 135.2 ppm.

14 Reagent **4** was obtained from the corresponding iminium salt by direct analogy with the dimethyl analogue, reported in reference 12.

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