An important application of the 1,8-diketone ring formation reaction: a concise synthesis of 5,6-diphenyl[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-thione and its coupling product

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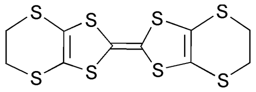
Syntheses of fully unsaturated 5,6-diphenyl[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-thione and its coupling product, a fully unsaturated analogue of BEDT-TTF, have been achieved by a 1,8-diketone ring formation reaction.

There has been wide interest in the synthesis of derivatives of bis(ethylenedithio)tetrathiafulvalene, BEDT-TTF (or ET) **1**.



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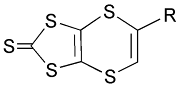
This is due to its electron donating ability, which makes it exhibit conducting and superconducting properties as charge transfer salts with electron acceptors such as TCNQ and mono anions.[1] The highest superconducting critical temperature, T_c, observed to date for an organic superconductor is 12.8 K with K-(BEDT-TTF)Cu[N(CN)$_2$Br].[2]

One of the important features, which has been the subject of efforts by various research groups, is the introduction of an increased conjugation, which would allow the system to have an extended π-electron delocalisation. So far, such an extension has been achieved in the middle of the molecule.[1b] However, there are limited examples of introduction of conjugation at the peripheral ethylene groups.[3]

Recently, we have reported a convenient method of synthesising fused 1,4-dithiin systems with various functional groups (**2**, **3**).[4] This method has allowed us to introduce four phenyl groups on to the peripheral ethylene bridges of BEDT-TTF, that is the synthesis of a tetra-phenyl substituted and fully unsaturated analogue, 5,5′,6,6′-tetraphenyl-2,2′bi([1,3]dithiolo[4,5-*b*][1,4]dithiinylidene) **11**, which has been the subject of research by other groups.[5] Unfortunately, their attempts have been unsuccessful so far, although trace amount of 5,6-diphenyl[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-thione **10** was claimed to have been obtained.[5c] We report here that our 1,8-diketone ring-closure reaction smoothly gives the precursor **10** in a relatively high yield, 65%, which proves that this reaction may be an important tool in the formation of fused and fully substituted 1,4-dithiin rings.



R = Ph, 4-CH$_3$OPh,
4-NO$_2$Ph, CH$_3$,[7] 4-BrPh[7]

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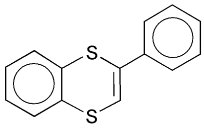

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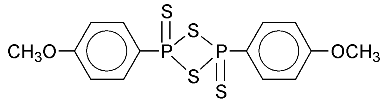

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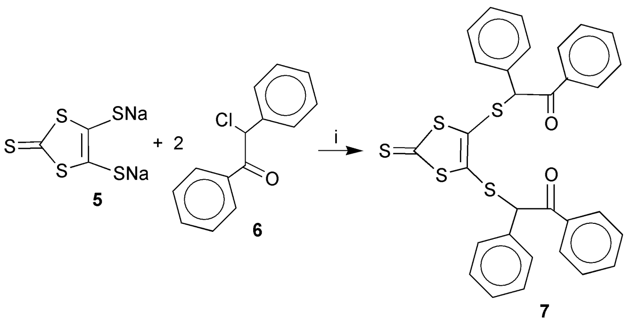
In our previous report,[4] we disclosed that refluxing the 1,8-diketones in toluene with Lawesson's Reagent (LR) **4** yielded fused thiophenes and 1,4-dithiins. The precursor **7**, which is the subject of the cyclisation reaction in this study, was easily obtained from the reaction of readily available dianion **5**[6] and desyl chloride† **6** in dry ethanol at rt in 90% yield (Scheme 1). Following the previous reaction conditions, the 1,8-diketone **7** was allowed to react with LR in boiling toluene overnight (Scheme 2). In agreement with the result reported by Noh *et al.*,[5b] fused thiophene rather than dithiin was isolated. Considering our preliminary results that such a ring formation reaction could be carried out with P_4S_{10} and tended to give 1,4-dithiin in a shorter reaction time, in another experiment, we treated **7** with P_4S_{10} in refluxing toluene.[7] Interestingly, this reaction, after 3 h reflux, gave **9** as one of the products, possessing a benzylphenyldithiole ring, along with the thiophene **8**, in 25 and 30% yields, respectively. This result suggested that, since there was no loss of sulfur, the initially *in situ* formed 1,4-dithiin derivative **10** rearranged radically to give benzylphenyldithiole **9**. Obviously, in the presence of sulfur as a source of radicals such a mechanism is likely. In view of all these experiences, cyclisation was performed with P_4S_{10} in refluxing toluene in the dark. After the consumption of starting material **7**, which took *ca.* 3 h, column chromatography of the crude reaction product (3 : 1, hexane–CH_2Cl_2) gave three compounds, thiophene **8** (20%), benzylphenyldithiole **9** (trace) and 1,4-dithiin **10**[8] (65%). The structures of **8**, **9** and **10** were confirmed by X-ray single-crystal diffraction analysis and the results will be published elsewhere.



Scheme 1 *Reagents and conditions*: i, EtOH (dry), N_2, rt, overnight.

With this fully unsaturated compound **10** in hand, which does not require storage under nitrogen, coupling product **11** was prepared following the well-established reaction scheme (Scheme 3). The thione sulfur atom in **10** was converted to oxygen with mercury acetate in a quantitative yield. Subsequent heating of the reaction product in neat triethylphosphite

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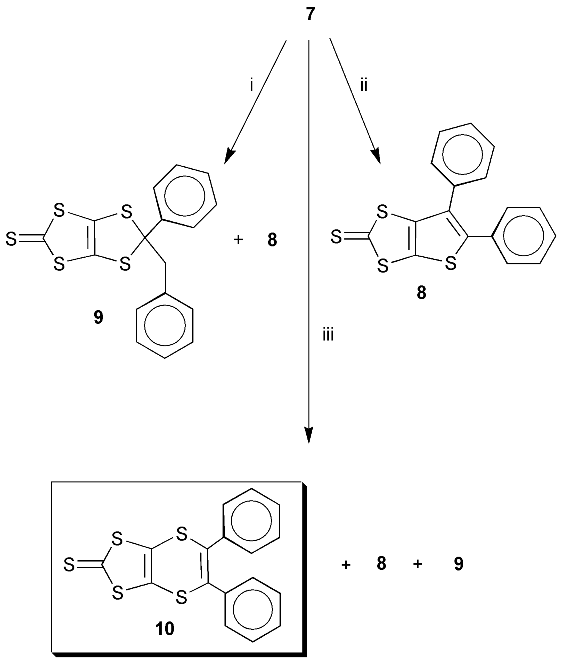
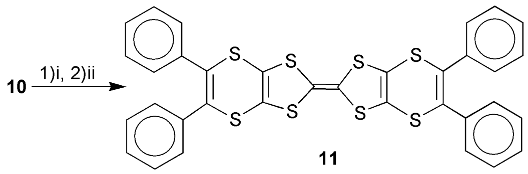


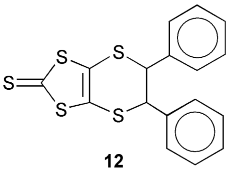
Scheme 2 *Reagents and conditions*: i, P_4S_{10}, toluene, reflux, 3 h; ii, LR, toluene, reflux, overnight; iii, P_4S_{10}, toluene, reflux, dark, 3 h.



Scheme 3 *Reagents and conditions*: i, $Hg(OAc)_2$–AcOH, $CHCl_3$, 3 h, rt; ii, $(EtO)_3P$, 110 °C, N_2, 2 h.

(110 °C) for 2 h resulted a yellow precipitate of **11**,[9] which was collected in 90% yield. Contrary to the result reported for the coupling of the saturated analogue **12**, which gave tetrakis(ethylthio)tetrathiafulvalene **13** rather than its self-coupled product **14**,[5a,c] the fully unsaturated **10** yielded **11** smoothly in a high yield. This result further suggests that unsaturated dithiin ring contributes to the stability of the molecule through conjugation.

In conclusion, we have demonstrated that a fully substituted and fused 1,4-dithiin derivative can easily be prepared by a 1,8-diketone ring-formation reaction, using P_4S_{10}, and also a fully unsaturated analogue of BEDT-TTF has been prepared in an efficient procedure and in a good yield. The precursor **10** and the analogue **11** themselves could prove useful as electronic materials.



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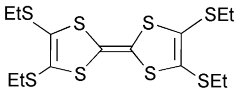

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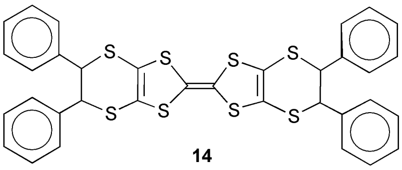

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Notes and references

† The IUPAC name for desyl chloride is 2-chloro-2-phenylacetophenone.

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7 T. Ozturk and F. Turksoy, unpublished results.
8 5,6-Diphenyl[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-thione **10**: mp 113–114 °C. HRMS *m/z* calculated 373.9386; measured 373.9397 for $C_{17}H_{10}S_5$. Calc. C 54.5, H 2.69; found C 54.44, H 2.66%. IR ν 1080 cm^{-1} (C=S). UV λ_{max} (CH_3CN) 391 nm. δ_H(250 MHz, $CDCl_3$) 7.09–7.34 (m, 10H). δ_H(67.8 MHz, $CDCl_3$) 213.9 (C=S), 136.2 (C-*q*), 134.7 (C-*q*), 129.9 (C-*q*), 129.5 (C-*t*), 128.7 (C-*t*), 128.6 (C-*t*).
9 5,5′,6,6′-Tetraphenyl-2,2′bi([1,3]dithiolo[4,5-*b*][1,4]dithiinylidene) **11**: mp 249 (decomp.). HRMS *m/z* calculated 683.9330; measured 683.9329 for $C_{34}H_{20}S_8$. Calculated C 59.6, H 2.9; found C 59.71, H 2.79%. δ_H(250 MHz, $CDCl_3$) 7.14–7.30 (m, 20H). δ_c(67.8 MHz, $CDCl_3$) 136.8 (C-*q*), 135.3 (C-*q*), 134.2 (C-*q*), 129.6 (C-*t*), 128.8 (C-*t*), 128.4 (C-*t*).