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Tetrahedron Letters 45 (2004) 5103–5107
Tetrahedron Letters

Synthesis of BEDT-TTF derivatives with carboxylic ester and amide functionalities

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Received 20 February 2004; revised 22 April 2004; accepted 29 April 2004

Abstract—Synthetic routes to BEDT-TTF derivatives bearing side chain carboxylic ester and amide groups are reported. Methyl ET-ethanoate was prepared in five steps from vinylacetic acid; amide groups were installed early in the synthesis by mixed anhydride methods before the final coupling reaction.
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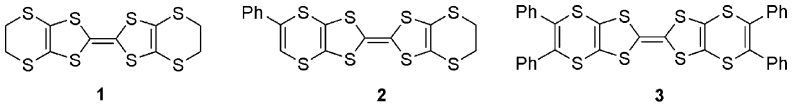
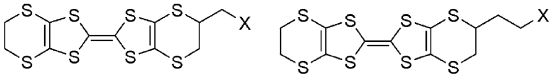
1. Introduction

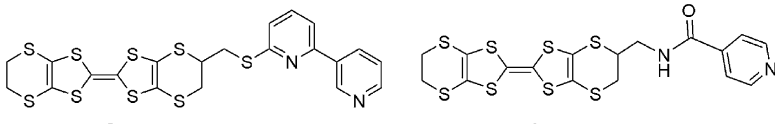
The organosulfur donor BEDT-TTF **1**, also known as ET, has played an important role in the development of electroactive organic materials.[1] It forms a very wide range of radical cation salts with conducting, semiconducting and superconducting properties.[2,3] ET has been co-crystallised and electrocrystallised with C_{60},[4] and it has been used to prepare radical cation salts with magnetic anions to produce a paramagnetic superconductor and ferrimagnetic and paramagnetic semiconductors.[5] Despite the interest in using ET for these studies, there has been a gradually increasing amount of work on the preparation and study of substituted ETs. The synthesis and radical cation salts of the chiral tetramethyl derivative were reported 15 years ago,[6] and results from the tetraethyl derivative (TEET) have been published recently.[7] Indeed, the charge transfer compound (TEET)Ni(dmit)$_2$ is being evaluated as a molecular ruler for nanotechnology. Ozturk has prepared unsaturated phenyl[8] and tetraphenyl[9] derivatives of ET, **2** and **3**, and poly-chloro and -fluoro analogues of ET



1 **2** **3**



4 X = OH
5 X = NH_2
6 X = OH
7 X = NH_2



8 **9**

Keywords: Organosulfur donors; Hydrogen bonding; BEDT-TTF; Amides.
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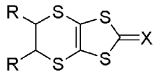
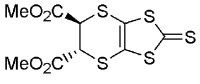
doi:10.1016/j.tetlet.2004.04.176

have been prepared by Fourmigue as isomeric mixtures.[10] We have prepared hydroxymethyl and hydroxyethyl derivatives **4**[11] and **6**,[12] the corresponding amino compounds **5**[13] and **7**[13] and other polyhydroxy functionalised systems.[14] The increasing interest in bifunctional materials,[15] has led us to incorporate metal binding groups,[12] for example, **8** and **9** and chiral moieties[16] on to the ET framework. To widen the scope for attachment of such groups to the ET system we now report results on the preparation of ETs functionalised with carboxylic ester and amide functionalities. Furthermore, amide groups will introduce hydrogen bonding into the system, of particular interest for ordering the anions in their radical cation salts.

ETs are usually prepared by coupling reactions of thiones or oxo compounds **10** or **11**. However, direct attachment of a carboxylic ester or nitrile to these systems led to the attempted coupling reactions mediated by triethyl phosphite failing, for example, for the thiones **12**[17] and **13**.[18] The ring carbon atom is activated to nucleophilic attack by the electron withdrawing properties of the carbonyl and this can lead to Arbuzov reactions with triethyl phosphite yielding tetra(ethylthio)TTF. So the syntheses of materials with a methylene group between the ET and carboxyl function were targeted.



10 X = S
11 X = O



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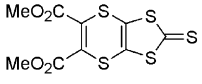
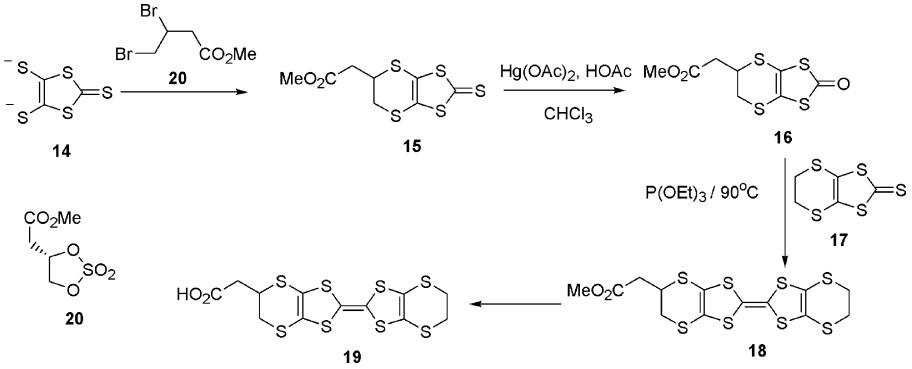


13

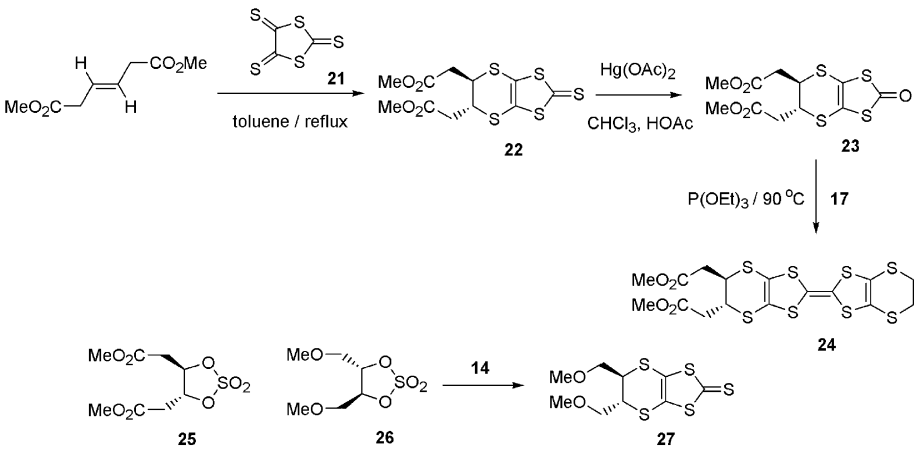
Dithiolate **14**, prepared by deprotection of its dibenzoyl derivative with sodium methoxide, was reacted with methyl 3,4-dibromopropionate, obtained from vinylacetic acid in two steps,[19] to give a precipitate of the thione **15** in 72% yield. Conversion to the oxo compound **16** using the standard procedure with mercuric acetate and coupling with the unsubstituted thione **17** in triethyl phosphite afforded the novel donor **18**[20] in a 35% yield from thione **15** (Scheme 1). The reactions were clean and efficient, and chromatography was only required at the final step to separate the desired donor from homo-coupled products. Thus, racemic donor **18** is a readily accessible molecule for the organic materials community. Conditions for hydrolysing the ester to the acid **19** without decomposing the molecule were not easy to establish. This was achieved finally with potassium hydrogen carbonate in a THF/methanol/water mixture to give a fine powder after drying in 75% yield. The enantiopure version of the donor **18** has also been prepared; the key step is reaction of the dithiolate **14** with the cyclic sulfate ester **20** and will be reported with the synthesis of other chiral ET derivatives.[16]

The related donor, which carries two vicinal, *trans* oriented, $-CH_2CO_2Me$ side-chains has also been prepared. In this case the corresponding thione **22** was prepared by the hetero Diels–Alder reaction of the trithione **21** with dimethyl *E*-hex-3-endioate in 55% yield (Scheme 2). Such reactions of trithione **21** were reported by Neilands et al.[21] and we have applied it to the synthesis of a number of such thiones.[12,13,16] The thione was converted to the oxo compound **23**, which was coupled with the unsubstituted thione **17** to give the disubstituted donor **24** in a yield of 29%. In contrast, reaction of the disubstituted cyclic sulfate ester **25** with the dithiolate **14** gave only a trace of thione. Only two small substituents on the cyclic sulfate ester are consistent with satisfactory yields of the corresponding thiones,[11] for example, the bis(methoxymethyl)-substituted thione **27** was prepared in only ca. 5% yield from cyclic sulfate ester **26**.

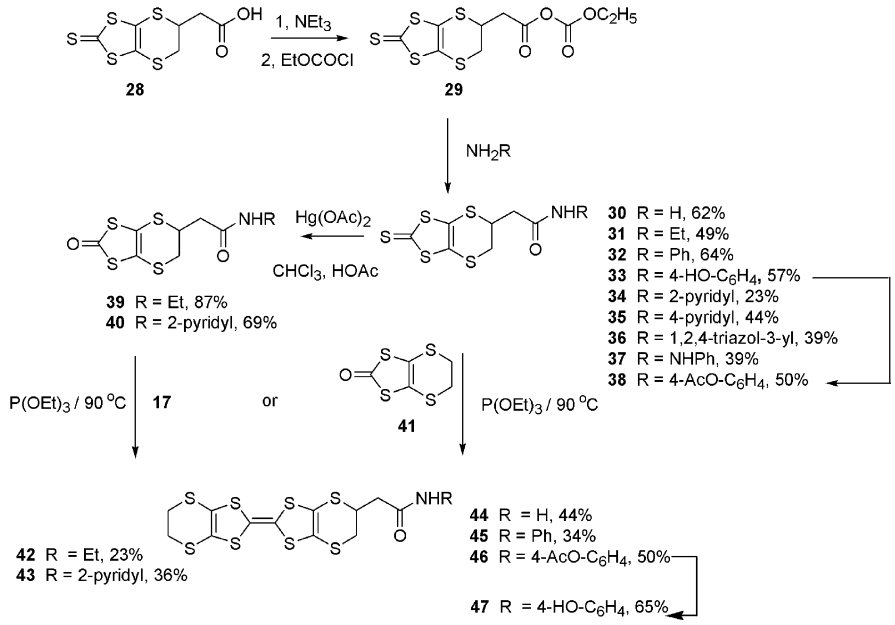
To prepare amide derivatised ETs it was found best to install the amide group early in the synthesis, since direct reaction of donor **18** with amines to give amides was unsuccessful, and the initial attempts to use acid **19** were not promising, partly due its low solubility in common organic solvents. Thus, cycloaddition of vinylacetic acid and trithione **21** in refluxing toluene, followed by removal of polymeric material by chromatography and distillation of residual vinylacetic acid afforded carboxylic acid **28** as a brown solid in 56% yield. The alternative approach to **28** by reaction of 3,4-dibromobutanoic acid and the dithiolate **14** proved unsuccessful. Amides were prepared using mixed anhydride chemistry (Scheme 3). Thus carboxylic acid **28** was converted to mixed anhydride **29** by treatment with ethyl chloroformate and triethylamine in THF under nitrogen at 0 °C. In situ treatment with an amine followed by stirring overnight



Scheme 1.



Scheme 2.

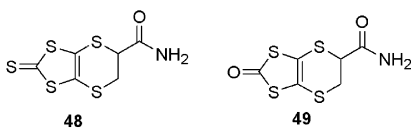


Scheme 3.

at room temperature and chromatography yielded the amides as yellow solids. Thus, using ammonia, ethylamine, aniline, 4-aminophenol, 2-amino- and 4-aminopyridine, or 3-amino-1,2,4-triazole gave the amide functionalised thiones **30**–**36** in 23–64% yields. Furthermore, reaction with phenyl hydrazine gave the hydrazide **37**. The hydroxyl group of thione **33** was then protected as an acetate to give thione **38**, prior to conversion to an ET derivative.

The thiones were converted into their corresponding donors, usually pink or orange solids, by one of two methods. Three thiones **30**, **32** and **38** were coupled directly with the unsubstituted oxo compound **41** to give donors **44**,[22] **45**[23] and **46** in 34–50% yield. A further two thiones, **31** and **34**, were converted to their oxo compounds **39** and **40**, which were then coupled with the unsubstituted thione **17** to give donors **42**[24] and **43**.[25] The lower overall yields for conversion of thione to donor via their oxo compounds (20–24%) suggest that preparation by coupling of the substituted thione may be preferable. Thiones **35**, **36** and **37** failed in the coupling reactions with **41**, possibly due to triethyl phosphite breaking the bond to the nitrogen of the amide group, generating amide anions, which could attack the dithiin ring.

We prepared thione **48** with an amide group attached to the ring skeleton by cycloaddition of trithione **21** and acrylamide in 43% yield and converted this material to the oxo compound **49**. However, attempted reaction of **48** or **49** with the unsubstituted oxo compound **41** or thione **17**, respectively, in triethyl phosphite gave no ET-carboxamide.



Thus a range of amide substituted organosulfur donors, with a variety of hydrogen bonding possibilities, is now available for conversion to radical cation salts. The 4-acetyloxyphenylamide **46** was hydrolysed to give the donor **47**, which has both a N–H and an O–H donor. Donor **43** is of interest since it has the potential for binding a metal cation at the pyridyl side chain. The cyclic voltammetries[26] of the novel ET derivatives showed two reversible oxidation peaks: **42**–**45** at very similar potentials to ET (0.48 and 0.89 V), and **18** (0.50 and 0.91 V) and **24** (0.52 and 0.94 V) at slightly higher values. Preliminary electrocrystallisation experiments have produced several microcrystalline salts.

Acknowledgements

We thank the EPSRC and Nottingham Trent University for studentships (R.J.B. and J.P.G.) and the EPSRC Mass Spectrometry Service for measurements. We thank the Chemistry Department, University of Warwick for help with several spectroscopic measurements.

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20. Compound **18**: Mp 149–150 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 4.03 (1H, m, 5-*H*), 3.73 (3H, s, O*CH*$_3$), 3.33 (1H, dd, $J = 13.2$, 3.1 Hz, 6-H_α), 3.29 (4H, s, 5′, 6′-H_2), 3.14 (1H, dd, $J = 13.2$, 5.6 Hz, 6-H_β), 2.84 (2H, d, $J = 6.9$ Hz, C*H*$_2$CO); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ: 170.8 (*C*=O), 113.8, 113.5, 112.7, 112.0, 111.4 (sp^2-*C*), 52.1 (O*C*H$_3$), 39.4 (*C*H$_2$CO), 38.6 (5-*C*) 34.7 (6-*C*), 30.2 (5′-, 6′-*C*); ν_{max} /cm^{-1} (KBr) 2947, 1730, 1432, 1303, 1253, 1202, 1014, 772. Found C, 34.3; H, 2.6%, $C_{13}H_{12}O_2S_8$ requires C, 34.2; H, 2.7%.
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22. Compound **44**: Mp 184–185 °C (dec); ^{1}H NMR (DMSO-d_6) δ: 7.49 (1H, br s, N*H*), 6.84 (1H, br s, N*H*), 4.14 (1H, m, 5-*H*), 3.31 (4H, s, 5′-, 6′-H_2), 3.30 (1H, dd, $J = 13.4$, 5.7 Hz, 6-H_α), 3.20 (1H, dd, $J = 13.4$, 3.2 Hz, 6-H_β), 2.62 (2H, d, $J = 7.2$ Hz, C*H*$_2$CO); ^{13}C NMR (67.8 MHz, DMSO-d_6) δ: 169.5 (*C*=O), 112.4, 111.7, 110.4 (sp^2-*C*), 39.3 (*C*H$_2$CO), 38.9 (5-*C*), 33.1 (6-*C*), 28.3 (5′-, 6′-*C*); ν_{max}/cm^{-1} (KBr) 3379, 3180, 2918, 2855, 1655, 1625, 1407, 1264, 908, 770, 609; HRMS (EI): found: 440.8613 $(M+H)^+$, $C_{12}H_{11}NOS_8 + H^+$ requires: 440.8606.
23. Compound **45**: Mp 196–197 °C; ^{1}H NMR (270 MHz, DMSO-d_6) δ: 7.57 (2H, d, $J = 8.4$ Hz, 2 × Ar-*H*), 7.29 (2H, t, $J = 8.3$ Hz, 2 × Ar-*H*), 7.04 (1H, t, $J = 8.3$ Hz, Ar-*H*), 4.23 (1H, m, 5-*H*), 3.38 (2H, m, 6-H_2), 3.32 (4H, s, 5′-, 6′-H_2), 2.88 (2H, m, 6-C*H*$_2$CO); ^{13}C NMR (67.8 MHz, DMSO-d_6) δ: 167.7 (C=O), 138.8, 128.7, 123.3, 119.1 (6 × Ar-*C*), 112.8 (sp^2-*C*), 41.5 (*C*H$_2$CO), 38.1 (5-*C*), 34.4 (6-*C*), 29.5 (5′-, 6′-*C*); ν_{max}/cm^{-1} (KBr) 3049, 2966, 2920, 2849, 1654, 1596, 1522, 1497, 1442, 1410, 1311, 1284, 1256, 888; HRMS (EI): found: 516.8930 $(M+H)^+$, $C_{18}H_{15}NOS_8 + H^+$ requires: 516.8919.
24. Compound **42**: Mp 170–171 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 5.55 (1H, br s, N*H*), 4.10 (1H, m, 5-*H*), 3.37 (1H, dd, $J = 13.4$, 3.0 Hz, 6-H_α), 3.30 (2H, m, NHCH_2), 3.29, (4H, s, 5′-, 6′-H_2), 3.13 (1H, dd, $J = 13.4$, 5.0 Hz, 6-H$_\beta$), 2.61 (2H, m, C*H*$_2$CO), 1.13 (3H, t, $J = 7.3$ Hz, NH-CH$_2$C*H*$_3$); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ: 168.5 (*C*=O), 113.9, 111.3 (sp^2-*C*), 41.6 (*C*H$_2$CO), 38.5 (5-*C*), 34.8 (6-*C*),

34.6 (NH-CH_2), 30.2 (5′-, 6′-*C*), 14.8 ($NHCH_2CH_3$); ν_{max}/cm^{-1} (KBr) 3424, 3281, 2972, 2922, 1633, 1560, 1408, 1284, 1253, 1105, 774. Found C, 35.5; H, 3.2; N, 2.9%, $C_{14}H_{15}ONS_8$ requires C, 35.8; H, 3.2; N, 3.0%.

25. Compound **43**: Mp 129–131 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 8.87 (1H, br s, N*H*), 8.27 (1H, dd, $J = 5.0$, 1.0 Hz, 6″-*H*), 8.19 (1H, dd, $J = 8.2$, 0.5 Hz, 3″-*H*), 7.72 (1H, dt, $J = 8.2$, 1.8 Hz, 4″-*H*), 7.07 (1H, ddd, $J = 7.3$, 5.0, 0.8 Hz, 5″-*H*), 4.20 (1H, m, 5-*H*), 3.41 (1H, dd, $J = 13.4$, 2.9 Hz, 6-H_α), 3.29 (4H, s, 5′-, 6′-H_2), 3.21 (1H, dd, $J = 13.4$, 2.9 Hz, 6-H_β), 2.92 (2H, d, $J = 7.0$ Hz, CH_2CO); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ: 168.2 (*C*=O), 151.3, 147.6, 138.7, 120.2, 114.7 (5 × Ar-*C*), 113.9, 113.8, 112.4, 112.1 (sp^2-*C*), 42.2 (CH_2CO), 37.9 (5-*C*), 35.2 (6-*C*), 30.2 (5′-, 6′-*C*); ν_{max}/cm^{-1} (KBr) 2967, 2920, 2850, 1684, 1654, 1577, 1434, 1302, 774; HRMS (ES): found: 518.8949 $(M+H)^+$, $C_{17}H_{14}N_2OS_8 + H^+$ requires: 518.8950.

26. Data measured in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate under nitrogen, with a scan rate of 100 mV s^{-1}, quoted relative to Ag/AgCl.