

Synthesis and crystal structure of 4,7-bis(2-thienylethynyl)-2,1,3-benzothiadiazole[†]

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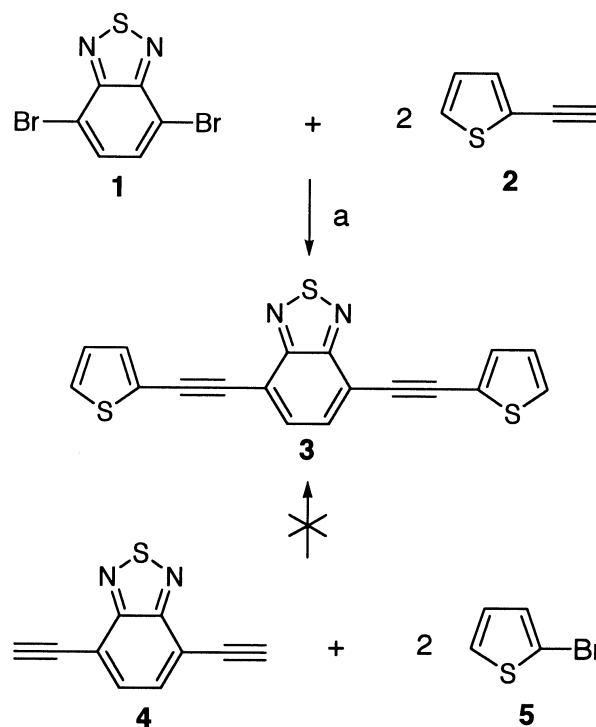
4,7-Bis(2-thienylethynyl)-2,1,3-benzothiadiazole was prepared by Sonogashira coupling. The crystal structure showed that one thiophene ring is coplanar and the other is perpendicular to the benzothiadiazole ring.

Keywords: Sonogashira coupling, thiophene, 2,1,3-benzothiadiazoles, alkyne, molecular electronics

Synthesis of well-defined mono-disperse conjugated oligomers has become important due to their electronic, optical and opto-electronic functions.¹ Recently such oligomers themselves not only attract much interest as models of polymers but also are expected to be promising molecular wires in a new field of molecular-scale electronics.² In order to elucidate the structure-property relationship of such oligomers, many efforts have been paid to their synthesis. Among them, there are a number of reports on oligo(1,4-phenylene ethynylene)s as the oligomers toward molecular wires probably due to their comparatively easy synthesis. However, oligo(1,4-phenylene ethynylene)s are insufficient as molecular wires owing to their relatively large HOMO-LUMO gaps, which may lead to unsatisfactory electric conduction. In recent years, we have synthesised co-oligomers and co-polymers³ composed of alternating donor-acceptor aromatic heterocycles showing small HOMO-LUMO energy gaps⁴ responsible for their unique electronic and chemical properties. As an extension of this research, we undertook the synthesis of new ethyne-linked alternating oligomers consisting of thiophene (donor) and 2,1,3-benzothiadiazole (acceptor) rings. We report here the synthesis of a new donor-acceptor-donor “trimer” with ethyne linkages, and its crystal structure.

For the purpose of incorporation of ethyne units, Sonogashira cross-coupling⁵ of aryl halides and ethyne termini in the presence of Pd and Cu catalysts has been most frequently employed because of the practical ease and mild reaction conditions. We considered two approaches to obtain compound **3**. One way is by the cross-coupling of one acceptor-heterocyclic dihalide, 4,7-dibromo-2,1,3-benzothiadiazole (**1**), and two donor-heterocyclic ethynes, 2-ethynylthiophene (**2**), and another is the combination of one acceptor-heterocyclic diethyne **4** and two donor-heterocyclic halide molecules **5** (Scheme 1). When we attempted the latter reaction, the coupling did not proceed and gave only a black insoluble solid. On the other hand, cross-coupling of **1** with 2 moles of **2** using PdCl₂(PPh₃)₂ and CuI catalysts in Et₃N-THF⁸ under reflux yielded the bis-coupling product **3** in 67% yield (Scheme 1).⁹

In order to investigate the molecular structure of **3**, an X-ray analysis was carried out. The molecular structure of **3** is shown in Fig. 1. Because of the 180° rotation of thiophene rings, the thiophene units were disordered in the crystal and the S and C atoms were averaged in the process of X-ray



a. PdCl₂(PPh₃)₂, CuI, THF-Et₃N, reflux, 67%

Scheme 1

solution. The molecule shows a unique structure. The two dihedral angles between the central 2,1,3-benzothiadiazole and terminal thiophene rings were found to be 2.5° and 89.9°, indicating that one thiophene ring and the benzothiadiazole moiety are coplanar, while the other thiophene ring is perpendicular to this plane. Interestingly, the crystal structure of **3** shows a tape-like planar packing arrangement of **3** and adopts a herringbone structure. (Fig. 2) The intermolecular interaction is characterised by short intermolecular S...N contacts between benzothiadiazole-faced thiophene and benzothiadiazole rings. The distance between the S of the disordered thiophene and the N of the thiadiazole (3.27 Å) is shorter than the van der Waals distances (3.35 Å). The tape-like planes are aligned in the *b*-axis direction. The distance between the tape-like planes is 3.54 Å and no π -stack is formed in the crystal. We cannot suggest a reason for the unique crystal packing

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[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

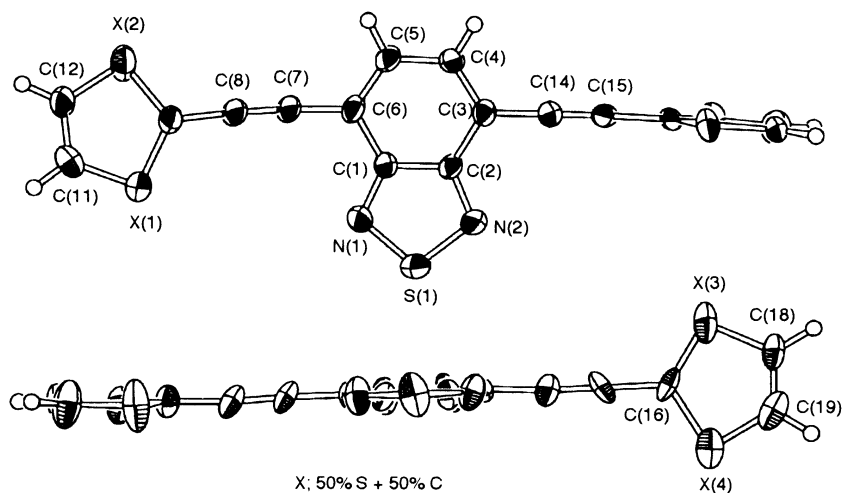


Fig. 1 Molecular structure of **3** in the crystal, showing top (upper) and side (lower) views.

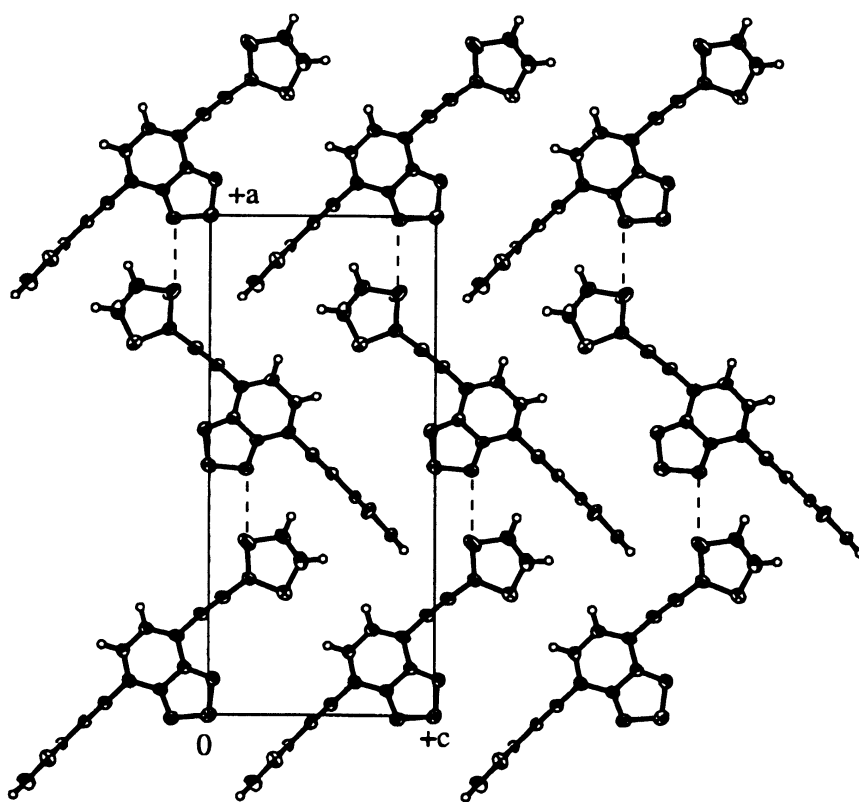


Fig. 2 Packing diagram of trimer **3** along the crystallographic *b*-axis.

mode at present. It is unexpected that one thiophene ring is perpendicular to the rest of the molecular plane.

Physical properties of the trimer **3** were also investigated by spectroscopic and electrochemical methods. The absorption band of the trimer (λ_{max} 435 nm) was observed at longer wavelengths, compared with other ethyne-linked oligomers consisting of mono aromatic cycle.¹⁰ This shows that our molecular design is effective to obtain low-HOMO–LUMO-gap oligomers. The cyclic voltammogram of **3** showed an electrochemically amphoteric system. Thus, an irreversible oxidation wave (peak potential, 1.58 V vs SCE) and a reversible reduction wave (half wave potential, –1.06 V vs SCE) were observed. The former can be assigned to an oxidation process of the donor thiophene moiety and the latter can be regarded as

a reduction behavior of the acceptor 2,1,3-benzothiadiazole. Polymerisation by electrochemical oxidation was not found in this ethyne-linked trimer system.

Experimental

Melting points were determined on a Yanaco Melting Point apparatus and are uncorrected. IR spectra were taken on a JASCO FT/IR-5M spectrometer (KBr pellets). ¹H and ¹³C spectra were recorded on a Bruker DRX500 spectrometer. MS spectra were obtained on a Shimadzu QP-1000EX. High resolution mass spectra were determined in the Analytical Section of Tokyo Institute of Technology under the direction of Dr Yukiko Muramatsu. Column chromatography was performed using Wakogel C300 silica gel. All reactions were performed under nitrogen.

Preparation of compound 3: Et₃N (0.4 ml) was added to a mixture of 4,7-dibromo-2,1,3-benzothiadiazole⁶ (134 mg, 0.45 mmol) and 2-ethynylthiophene⁷ (114 mg, 1.05 mmol), PdCl₂(PPh₃)₂ (17 mg, 5 mol% based on dibromide) and CuI (9 mg, 15 mol% based on dibromide) in THF (5 ml). The reaction mixture was refluxed for 2 h. It was poured into water and extracted with CHCl₃. The combined organic layer was washed with brine and dried over Na₂SO₄. After removal of the solvent, the residue was purified by twice column chromatography on silica gel (CHCl₃/hexane, 1:1) to give 4,7-bis(2-thienylethynyl)-2,1,3-benzothiadiazole **3** (106 mg, 67%) as an orange solid, m.p. 196–200°C (dec.); IR (KBr) 2358, 2205, 1728, 1484, 1418, 1331, 1219, 834, 728, 718, 704 cm⁻¹; ¹H NMR (CDCl₃) δ 7.07 (dd, *J* = 3.8, 5.0 Hz, 2H, 4-ThH), 7.39 (d, *J* = 5.0 Hz, 2H, 5-ThH), 7.46 (d, *J* = 3.8 Hz, 2H, 3-ThH), 7.77 (s, 2H, ArH); ¹³C NMR (CDCl₃) δ 89.11 (*C* ≡ *C*), 90.88 (*C* ≡ *C*), 116.95, 122.45, 127.37, 128.65, 133.21, 133.28, 154.12; MS (EI) *m/z* (%) 348 (100) [M]⁺; HRMS (EI) *m/z*: calcd for C₁₈H₈N₂S₃ 347.9850, found 347.9817.

Crystal data for 3: C₁₈H₈N₂S₃, *M* = 348.45, orthorhombic, space group *P*2₁2₁2, *Z* = 4, *a* = 22.188(2), *b* = 7.067(2), *c* = 9.805 (1) Å, α = β = γ = 90°, *V* = 1537.4 (4) Å³, *D*_c = 1.51 g cm⁻³, μ = 4.80 cm⁻¹, *T* = 296K. An orange prism prepared by slow evaporation from THF and chloroform was used for data collection reflections with a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71070 Å) from a rotating-anode generator operating at 50 kV and 200 mA. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 23.6 < 2θ < 29.0°. A total of 1924 reflections was collected. The intensities of three representative reflections were measured after every 150 reflections and showed no significant intensity variation during the data collection. No decay correction was applied. The data were corrected for Lorentz and polarisation effects. The structure was solved by direct methods¹¹ and expanded using the Fourier technique.¹² Because of a 180°-rotational disorder, the geometrical parameters of the thiophene rings are less reliable. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1260 observed reflections (*I* > 2σ(*I*)) and 209 variable parameters and converged with *R* = 0.044 and = 0.041. All calculations were performed with the teXsan for Windows.¹³ Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors. *J. Chem. Res. (S)*, 2002, Issue 2. CCDC 173920.

This work was supported by the Joint Studies Program of the Institute for Molecular Science, and by the fund of Himeji Institute of Technology.

Received 20 November 2001; accepted 24 April 2002
Paper 01/1143

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