

Synthesis of Benzotrifuran and Benzotripyrrole Derivatives and Molecular Orientations on the Surface and in the Solid State

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Dedicated to Professor Chunli Bai on the occasion of his 60th birthday

Abstract: We developed a concise synthetic method for benzotrifurans and benzotripyrroles from 1,3,5-triethynyl-2,4,6-trifluorobenzenes by one-pot reactions in good to excellent yield. By investigating 2-D and 3-D structures of a variety of benzotrifuran and benzotripyrrole derivatives using scanning tunneling microscopy (STM) and singlecrystal X-ray diffraction techniques, we

Keywords: cyclization • heterocycles • scanning tunnel microscopy • solid-state structures • X-ray diffraction found both similarities and dissimilarities. We also found that diverse molecular 3-D orientations were derived in their single crystals according to substituents on the molecules and that the emission properties in the solid state are dependent on their packing manners.

Introduction

As chemists' interest rapidly shifts from the properties of a single molecule to those of molecular solids as found in organic photoelectronic applications,^[1] there is an increasing interest in the 3-D hierarchical organization of organic molecules in the solid state,^[2] as well as in the 2-D organization at an interface on which a new 3-D structure evolves.^[3] For the potential readiness to form compact crystalline or liquid crystalline packing structures and for octopolar properties, three-fold symmetric planar molecules have attracted considerable attention,^[4–7] for their utility in nonlinear optics,^[8] organic electronics,^[9] discotic liquid crystals,^[10] self-organization,^[11] and host–guest chemistry.^[12] Because of the synthetic availability, all-carbon molecular skeletons such as triphenylene, truxene, and hexabenzocoronene have been widely employed and used as a foundation to attach long alkoxy chains on their periphery. We considered that C_{3h} -symmetric molecules composed of three furans and pyrroles may have enhanced octopolar properties compared with the corresponding all-carbon congeners, and may be able to achieve better control of the molecular organization. The latter idea was conceived because of the utility of the less complicated congeners, benzodifurans and benzodipyrroles, in organic electronics applications.^[13] We report herein the development of an expeditious synthesis of a variety of C_3 -symmetric benzotrifurans (BTFs) and a new class of compounds, benzotripyrroles (BTPs), in two steps from readily available 1,3,5-trifluoro-2,4,6-triiodobenzene (Scheme 1).^[14] The key



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Scheme 1. Synthesis of benzotrifurans and benzotripyrroles. DIPA, diiso-propylamine.

step is the coupling of a 1,3,5-triethynylbenzene^[8b] and a formal X^{2-} reagent, that is, water or a primary amine in the presence of cesium hydroxide or sodium hydride. We also describe the 2-D and the 3-D molecular packing and solid-state photophysical properties that reflect the molecular orientation on the surface and in the solid.^[15] **AN ASIAN JOURNAL**

Results and Discussion

The known syntheses of BTF derivatives rely either on intramolecular esterification^[16] or on condensation of polyphenols with benzoins,^[17] and often suffer from low yields or limited scope. We found that an alternative strategy via a 1,3,5-triethynyl-2,4,6-trifluorobenzene derivative, prepared by Sonogashira coupling between an acetylene and 1,3,5-trifluoro-2,4,6-triiodobenzene, provides an expeditious route to BTF with hydroxide. As shown in Table 1, the reaction of

Table 1. Synthesis of benzotrifurans via 1,3,5-triethynyl-2,4,6-trifluorobenzene derivatives.

	R ¹ F F F 1a-1j R ¹	∠R ¹ CsOH·H₂O (10 equiv) DMA reflux, 1 h	$R^{1} \qquad \qquad$	
Entry	\mathbb{R}^1	Substrate	Product	Yield [%]
1	Ph	1 a	2 a	95
2	2-Me-C ₆ H ₄	1b	2 b	79
3	3-Me-C ₆ H ₄	1c	2 c	92
4	$4-\text{Me-C}_6\text{H}_4$	1 d	2 d	84
5	$4 - C_5 H_{11} - C_6 H_4$	1e	2e	91
6	4-MeO-C ₆ H ₄	1f	2 f	75
7	$4-CF_3-C_6H_4$	1g	2 g	88
8	$4-Br-C_6H_4$	1 h	2 h	92
9	2-Py	1i	2i	77
10 ^[a]	tBu	1j	2j	41

[a] 20 equiv of CsOH·H₂O were employed.

1,3,5-triethynyl-2,4,6-trifluorobenzene with 10 equivalents of cesium hydroxide monohydrate in refluxing *N*,*N*-dimethyl-acetamide (DMA) furnishes BTF within 1 hour in a one-pot manner. For example, 1,3,5-trifluoro-2,4,6-tris(phenylethy-nyl)benzene (**1a**) afforded 2,5,8-triphenyl-BTF **2a** in 95%

Abstract in Japanese:

我々は、1,3,5-トリエチニル-2,4,6-トリフルオ ロベンゼンを出発物質としたワンポット反応に 基づく、ベンゾトリフランおよびベンゾトリピロ ール誘導体の簡便な合成法を開発した.本方法を 用いて合成した種々の誘導体の二次元および三 次元集積構造を、走査型トンネル顕微鏡および単 結晶 X 線構造解析により観測した.また、ベンゾ トリフランは置換基の違いに応じて多様な充填 構造を取り、その違いが固体発光特性に影響する ことも見出した. yield (Table 1, entry 1). The 2-, 3-, and 4-tolylethynyl-substituted substrates 1b-d gave BTFs 2b-d in isolated yields of 79%, 92%, and 84%, respectively (entries 2-4). Substrates possessing phenyl groups with longer alkyl chains, electrondonating methoxy groups, and electron-deficient trifluoromethyl groups (1e-g) also gave the products in 91%, 75%, and 88% yield, respectively (entries 5-7). Cesium hydroxide was the base of choice, while sodium hydroxide and potassium hydroxide gave the BTF 2f from the electron-rich substrate 1f in only 47% and 68% NMR yield, respectively, even after reacting for 24 hours.^[18] The bromine atoms of (4bromophenyl)ethynyl-substituted substrate 1h remained attached under the reaction conditions, and we obtained 2,5,8tris(4-bromophenyl)-BTF 2h in 92% yield (entry 8). Heteroaryl groups of the substrate 1i were also tolerated in the reaction, thus affording tris(2-pyridyl)-BTF 2i in 77% yield (entry 9). From 3,3-dimethyl-1-butynyl-substituted substrate 1j, 2,5,8-tri-tert-butyl-BTF 2j was obtained in moderate yield (41%) in the presence of 20 equivalents of cesium hydroxide monohydrate because the reaction stopped after the formation of the second furan ring (entry 10, benzodifuran was obtained as a side product).

Similar reaction conditions, other than the use of sodium amide in place of cesium hydroxide, led to synthesis of BTP derivatives via a triple cyclization reaction (Table 2). The re-

Table 2. Synthesis of benzotripyrrole derivatives.



Entry	\mathbb{R}^1	Substrate	\mathbf{R}^2	time	Product	Yield [%]
1	Ph	1a	Ph	1 h	3 a a	91
2	Ph	1a	C_8H_{17}	1 h	3 ab	91
3	Ph	1a	Су	1 h	3 ac	82
4	2-Me-C ₆ H ₄	1b	Ph	3 h	3ba	90
5	3-Me-C ₆ H ₄	1c	Ph	1 h	3ca	84
6	4-Me-C ₆ H ₄	1 d	Ph	1 h	3 da	82
7	4-MeO-C ₆ H ₄	1f	Ph	3 h	3 fa	83
8	$4-CF_3-C_6H_4$	1g	Ph	1 h	3 ga	97
9	4-Br-C ₆ H ₄	1h	Ph	1 h	3 ha	86
10	2-Py	1i	Ph	1 h	3 ia	78
11	<i>t</i> Bu	1j	Ph	1 h	3 ja	nd

action of phenylethynyl-substituted substrate **1a** in the presence of 10 equivalents of sodium hydride in excess aniline at 100 °C afforded 1,2,4,5,7,8-hexaphenyl-4,7-dihydro-1*H*-dipyrrolo[2,3-*e*:2',3'-*g*]indole (**3aa**) in 91 % yield (entry 1). This substrate also gave N,N',N''-trioctyl-BTP **3ab** and N,N',N''-tricyclohexyl-BTP **3ac** in 91 % and 82 % isolated yield by the reaction in octylamine and cyclohexylamine, respectively (entries 2 and 3). A variety of 1,3,5-tris(arylethynyl)-2,4,6-trifluorobenzenes, which afforded BTF derivatives, also gave BTPs by the reaction with aniline in more than 75 % yield (entries 3–10), although sterically hindered 2-tolylethynyl-

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substituted substrate **1b** (entry 4) and electron-rich (4-methoxyphenyl)ethynyl-substituted substrate **1f** (entry 7) required longer reaction times for full conversion. As the sole exception, 3,3-dimethyl-1-butynyl-substituted substrate **1j** did not give the corresponding BTP at all but afforded the doubly cyclized benzodipyrrole in almost quantitative yield (entry 11).

We next studied the 2-D and 3-D crystals of these molecules, and found that the parent compound Ph_3 -BTF **2a** offered us an interesting example where we can compare the similarities and dissimilarities of the molecular arrangement under 2-D and 3-D conditions. It is widely acknowledged that molecular assembly on solid surfaces is a cooperative result of the molecule–molecule interactions and molecule– substrate interactions, and the assembly in a 3-D crystal is an even more complex event.^[19]

We first describe the 2-D molecular arrangement of the Ph₃-BTF molecule **2a** as studied by scanning tunneling microscopy (STM). A monolayer of BTF **2a** was formed from an about 10^{-5} M solution in THF without the formation of bilayers or multilayers either on highly ordered pyrolytic graphite (HOPG) or on Au(111) surfaces. The molecules **2a** on HOPG formed only a porous honeycomb structure in terms of interdigitation of heads of neighboring molecules (Figure 1a and 1b), whereas they formed a polymorphic structure including the honeycomb structure on the Au(111) surface (Figure S1 in the Supporting Information) and a close-packed structure in which molecules are arranged in a head-to-tail manner. We suppose that the different assem-



Figure 1. STM images of the Ph₃-BTF monolayer. (a) Porous honeycomb structure of the Ph₃-BTF monolayer on the HOPG surface (scan area = $7 \times 7 \text{ nm}^2$, I = 702 pA; $V_{\text{bias}} = 540 \text{ mV}$) and (b) its proposed structural model. (c) Close-packed structure of the Ph₃-BTF monolayer on the Au-(111) surface (scan area = $7 \times 7 \text{ nm}^2$, I = 1.025 nA; $V_{\text{bias}} = -200 \text{ mV}$) and (d) its proposed structural model.

blies on HOPG and Au(111) surfaces result from differences in molecule–substrate interactions. On the HOPG surface, the molecule–substrate interactions are relatively weak and molecules form the porous honeycomb structure by optimizing intermolecular dipole–dipole interactions. On the Au-(111) surface, the molecule–substrate interactions are stronger than those on the HOPG surface, and hence the stability of the system depends on both the molecule–molecule and the molecule–substrate interactions. Moreover, charge transfer between the molecules and the substrate is expected, which will modify the chemical nature of the molecule and hence the molecule–molecule interactions, thereby resulting in a structure different from that observed for HOPG. Similar 2-D polymorphs on Au(111) have been reported in an STM and molecular modeling study.^[20]

We next discuss the X-ray crystallographic structure of molecule **2a** (Figure 2a). This molecule in a single crystal was found to be nearly planar with the dihedral angle between the BTF core and phenyl groups being less than 11°. They are stacked to form 2-D layers parallel to the *a*-*b* plane, where the molecules are arranged in a head-to-tail manner (blue and red) just as in one of the structures found on the Au(111) surface (Figure 1c). These layers are densely packed in a single crystal with an interlayer distance of 3.32 Å. We may consider that this strong π - π interaction between each layer is one of the factors that make the crystal packing similar to the 2-D arrangement found on the Au(111) substrate rather than to those on HOPG.

The 4-tolyl-substituted BTF **2d** (Figure 2b) is also almost planar with a dihedral angle between the BTF core and the phenyl groups of less than 7°. The packing showed that a one-dimensional head-to-tail layered structure with an interlayer distance of 3.43 Å still remains (blue and red). However, the neighboring layers are mutually crossed to each other, benefiting from the CH– π interaction, including the methyl groups.

The 2-methyl group inhibits the head-to-tail structure, and the 2-tolyl-substituted BTF **2b** (Figure 2c) showed an entirely different packing comprising a slipped stacking columnar structure with an intermolecular distance of 3.38 Å along the stacking direction. The crystal packing of the BTF possessing the long pentyl group, $(4-C_5H_{11}-C_6H_4)_3$ -BTF **2e**, is not controlled by $\pi-\pi$ stacking but is dominated by alkylalkyl interactions. Consequently, a very porous structure formed (Figure 2d).

The molecular structure of the tripyrrole BTP **3aa** (Figure 2e) was entirely different from those of BTF because the *N*-phenyl group stands perpendicular (dihedral angle of 67°) to the molecular plane.

We described above the extensive π - π stacking in the single crystal of Ph₃-BTF (**2a**) and of (4-Me-C₆H₄)₃-BTF (**2d**), and weaker interactions for (2-Me-C₆H₄)₃-BTF (**2b**) and (4-C₅H₁₁-C₆H₄)₃-BTF (**2e**). Thus, one would expect that the emission spectra of the former two in their solid state would be different from each other, while those of the latter two would not, because the photoexcited states of **2a** and **2d** are expected to interact most strongly with the π -stacked



Figure 2. Molecular and packing structures of (a) Ph₃-BTF **2a**, (b) (4-Me-C₆H₄)₃-BTF **2d**, (c) (2-Me-C₆H₄)₃-BTF **2b**, (d) (4-C₅H₁₁-C₆H₄)₃-BTF **2e**, and (e) Ph₆-BTP **3aa**.

neighbors in a solid. This was indeed the case. In Figure 3, we show the absorption (solid blue lines) and emission (solid red lines) spectra of each molecule in a dilute dichloromethane solution (ca. $10^{-5}-10^{-6}$ M). The absorption spectra of thin films of all four compounds (blue dashed lines) are slightly red-shifted by about 10 nm and broadened, as expected from stacking in the solid state. However, the emission spectra in the solid state (red dashed lines) were red-shifted significantly for 2a and 2d, as much as approximately 40 nm compared with those in dichloromethane, while those for 2b and 2e remained almost the same as those in dichloromethane; that is, the excited state of molecules 2a and 2d in the crystalline state interacts strongly with the neighboring molecules to form a new state with a smaller band gap. A similar large red-shift was also observed for 3aa, which also agrees with the stacking seen in a single crystal (Figure 2e). The observed dichotomy is in good agreement with the crystal structure shown in Figure 2. On the basis of the above analysis, we expect that the molecules of 2c for which we could not obtain suitable crystals would be π -stacked in the solid.

The electrochemical properties of BTFs and BTPs are not unexpected on the basis of the properties of the corresponding difurans and dipyrroles, which we reported previously.^[12] Thus, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements indicated that the first oxidation potentials of the BTFs range from 0.53 V (2f with the electron-donating methoxy group) to 0.96 V (2h with the electron-withdrawing trifluoromethyl group) versus Fc/ Fc⁺, and that the oxidation potential of BTP 3aa is shifted to the negative side (0.16 V) because the three pyrrole moieties donate an electron to the π -system. Thermogravimetric analysis showed that BTFs and BTPs are thermally very stable. A weight loss of 5% of the BTF and BTP derivatives occurred only at temperatures higher than 322°C and 421 °C, respectively (see the Supporting Information), probably owing to the rigidity of the σ -framework.



Figure 3. Absorption (blue lines) and emission (red lines) spectra of **2a–e** and **3aa** in dichloromethane (solid lines) and in the solid state (dashed lines).

Conclusions

In summary, we have developed a concise synthetic method for the synthesis of 2,5,8-trisubstituted BTFs and 1,2,4,5,7,8hexasubstituted BTPs that enables the formation of three rings in one pot from 1,3,5-triethynyl-2,4,6-trifluorobenzenes in good to excellent yield. STM and X-ray analyses of their 2-D and 3-D structures suggest that the information about their 2-D molecular arrangement provides us with an idea about the way we can control the 3-D arrangement in a solid. We found that crystal packing of BTFs affects the emission spectra; that is, the emission spectrum is substantially red-shifted and broadened when all of the molecules in a crystal are well π - π stacked. We made a similar observation of the agreement of the π - π stacking and the emission spectra for benzodifuran derivatives,^[21] and hence we believe that emission spectra may serve as a convenient indicator of the molecular stacking of benzofurans in the solid state. In light of the established utility of C_3 -symmetric planar disc-shaped aromatic molecules combined with that of fused furan and pyrrole derivatives in optoelectronic applications,^[12] we expect that BTF and BTP derivatives will find use as basic skeletons for the design of new organic materials.

Experimental Section

Synthesis of 2,5,8-triphenylbenzo[1,2b:3,4-b':5,6-b'']trifuran (**2***a*)

A mixture of cesium hydroxide monohydrate (3.3 g, 20 mmol) and 1,3,5-trifluoro-2,4,6-tris(phenylethynyl)benzene (860 mg, 2.0 mmol) in N,N-dimethylacetamide (20 mL) was stirred at reflux temperature for 1 h. After cooling to room temperature, water (20 mL) was added, and the organic layer was separated and extracted with dichloromethane (3×20 mL). After concentration in vacuo, purification by flash column chromatography on silica gel (dichloromethane/n-hexane 5:95) afforded 2a as a colorless solid (820 mg, 95 % yield). M.p. 304 °C (TG-DTA); ¹H NMR (500 MHz, CDCl₃): $\delta = 7.38$ (t, J = 7.5 Hz, 3H, ArH), 7.44 (s, 3H, ArH), 7.50 (dd, J=6.9, 7.5 Hz, 6H, ArH), 7.96 ppm (d, J=6.9 Hz, ArH); ¹³C NMR (125 MHz, 6H. CDCl₃): $\delta = 98.5$ (3C), 111.0 (3C), 124.5 (6C), 128.2 (3C), 128.9 (6C), 130.6 (3C), 146.1 (3C), 155.0 ppm (3C); MS (APCI+ ionization mode) 426 $[M]^+$; elemental anal. calcd (%) for C₃₀H₁₈O₃: C 84.49, H 4.25; found C 84.10, H 4.34.

Synthesis of 1,2,4,5,7,8-hexaphenyl-4,7dihydro-1H-dipyrrolo[2,3-e:2',3'g]indole (3 aa)

A mixture of sodium hydride (760 mg, 20 mmol, 63% dispersed in oil) and 1,3,5-trifluoro-2,4,6-tris(phenylethynyl)benzene (860 mg, 2.0 mmol) in aniline (20 mL) was stirred at 100 °C for 1 h. After cooling to room temperature, water (20 mL) was added, and the organic layer was separated and extracted with dichloromethane (5×20 mL). The combined organic layers were passed through a pad of silica gel (eluent: dichloromethane). After concentration in vacuo, purification by flash column chromatography on silica gel (dichloromethane/*n* hexane 1:9) afforded **3aa** as a colorless solid (1.2 g, 91% yield. M,p. 429°C (TG-DTA); ¹H NMR (500 MHz, CDCl₃): δ = 5.88 (s, 3 H, Ar*H*), 7.07-7.14 (m, 15H, Ar*H*), 7.48 ppm (brs, 15H, Ar*H*); ¹³C NMR (125 MHz, CDCl₃): δ = 127.9 (6C), 128.2 (3C), 128.5 (6C), 129.1 (6C), 129.7 (6C), 130.2 (3C), 133.2 (3C), 135.9 (3C), 140.1 ppm (3C); MS (APCI⁺) 651 [*M*]⁺; anal. calcd (%) for C₄₈H₃₃N₃: C 88.45, H 5.10, N, 6.45; found C 88.19, H 5.22, N 6.24.

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