Rotational isomerism involving an acetylenic carbon IV: synthesis and structure of bis(1,1′;3′,1″-terphenyl-2′-yl)ethynes: molecular design of sterically congested alkynes toward restricted rotation about acetylenic axis†

Shinji Toyota,* Taku Iida, Chinatsu Kunizane, Naoki Tanifuji and Yukihiro Yoshida
Department of Chemistry, Faculty of Science, Okayama University of Science, Ridaicho, Okayama 700-0005, JAPAN

The title diphenylethyne derivative with 4-methylphenyl (tolyl) groups at all the *ortho* positions was synthesized by the Stille or Sonogashira coupling from the corresponding iodide. The X-ray structure revealed that the two terminal phenyl groups at the sp carbons are twisted by 63° out of the coplanar conformation to avoid steric interactions between the tolyl groups. The relative stabilities of possible conformers were analyzed by the PM3 calculations. The axially chiral derivative with two methoxymethyl groups showed no evidence of restricted rotation about the acetylenic axis by VT NMR measurements, its barrier being less than 35 kJ mol⁻¹. The spectroscopic features and reactivities of this sterically congested alkyne are also described.

Introduction

In diphenylethyne derivatives, the internal rotation of two terminal ('axial') phenyl groups about the central $C(sp^2)$–C≡C–$C(sp^2)$ axis takes place rapidly because the two groups are sufficiently far apart. For example, experimental and theoretical investigations have shown that the barrier to internal rotation is only 2–3 kJ mol⁻¹ in diphenylethyne.[2,3] Although molecular mechanics calculations indicate that the rotation is slightly retarded by substituents on the phenyl rings,[4] experimental studies on the substituent effects on the rotational isomerism are quite limited. To obtain further structural information on this type of compound, we studied a sterically congested diphenylethyne **1** with 4-methylphenyl (tolyl) groups at all the *ortho* positions (Scheme 1). 1,1′;3′,1″-Terphenyl-2′-yl (*m*-terphenyl-2′-yl) groups, the substructures of **1**, have been utilized as sterically crowded ligands for the stabilization of unstable species[5] or other molecular designs.[6] A molecular model of **1** suggests that the 'wing' tolyl groups interact significantly with each other during the internal rotation of the axial phenyl groups about the acetylenic axis; therefore, we expected considerable enhancement of the rotational barrier as observed in the bis(9-triptycyl)ethyne system.[1,7,8]

Recently, pinwheel-shaped structures consisting of a linear rod with two large groups at both termini have been utilized in the design of molecules for molecular recognition and molecular machines, in which conformational changes of the terminal groups contribute significantly to the dynamic properties.[9–12] It is therefore necessary to understand the factors controlling conformational mobility and preference in **1** for use as an acyclic model of these functional molecules. Furthermore, if this molecule takes a staggered conformation about the acetylenic axis because of steric hindrance, the structure is extensible toward tetrahedral-like directions by the functionalization of the four methyl groups, as shown in **2**. In this paper we present the syntheses and structures of *m*-terphenyl based alkynes as well as the effects of steric hindrance on their spectroscopic properties and reactivities.

Results and discussion

Synthesis and spectroscopic properties

Compound **1** was synthesized by two coupling reactions, as shown in Scheme 2. Iodide **4**, a key precursor of the *m*-terphenyl synthesis, was obtained by the Hart reaction of **3** with a Grignard reagent.[13,14] Compound **4** was converted into the terminal alkyne **5** by Sonogashira coupling[15] with (trimethylsilyl)ethyne followed by desilylation. Although the Sonogashira coupling of **4** and **5** afforded **1**, the isolated yield (44%) is low because of the formation of 1,3-butadiyne, a dimer of **5**, and some separation problems. Stille coupling of iodide **4** and bis-
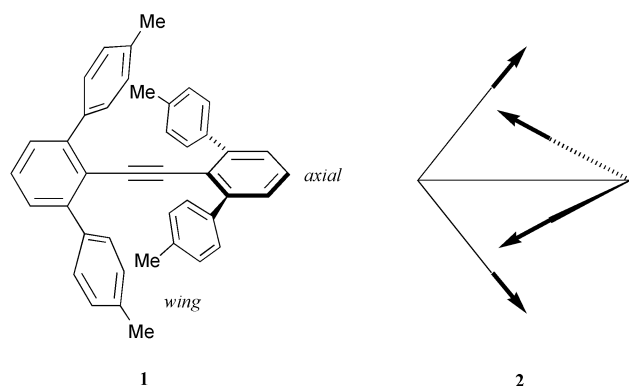
Scheme 1
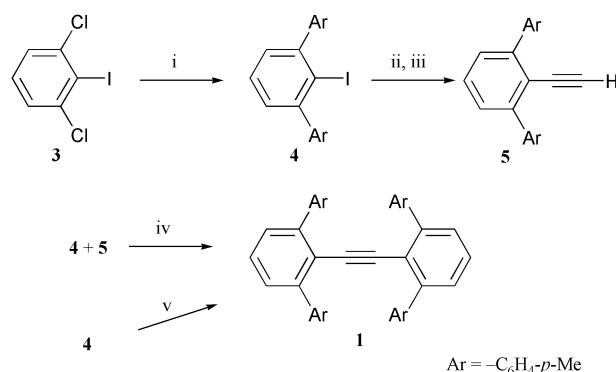
Scheme 2 *Reagents and conditions*: i. ArMgBr, THF, then I₂; ii. Me₃SiC≡CH, PdCl₂(PPh₃)₂, CuI, THF–NEt₃; iii. Bu₄NF, THF; iv. PdCl₂(PPh₃)₂, CuI, PPh₃, THF–NEt₃.; v. Bu₃SnC≡CSnBu₃, Pd(PPh₃)₄, LiCl, dioxane.

Ar = –C₆H₄-*p*-Me

† Part 3. See ref. 1.

(tributylstannyl)ethyne gave a better result, the pure material being readily isolated in 63% yield.[16]

The ^{13}C NMR signal due to the acetylenic carbons in **1** was observed at δ 93.8, being slightly shifted downfield compared with the diphenylethyne signal (δ 89.6).[17] In the X-ray structure to be shown later, the sp carbons lie around the border of shielding and deshielding regions of ring currents induced by the four tolyl groups. Therefore, the observed deshielding may be attributed to the decrease in conjugation in the diphenylethyne unit arising from the staggered conformation.[18] The UV spectra of **1** and related compounds are shown in Fig. 1. Compound **1** shows a relatively intense band at 258 nm with a shoulder extending to 330 nm. Bands with complicated structures at 260–300 nm, which are typical for diphenylethyne, were not observed for **1**. The absorption band around 250 nm (*p* band of the benzene chromophore) is red-shifted in the order of **4**, **5**, and **1** by 10–20 nm each. This trend indicates that one terphenyl unit electronically interacts not only with the attached acetylene unit but also with the other terphenyl unit through the acetylenic axis; namely, the acetylene moiety in **1** functions as a conjugate linker, and the whole molecule may be a conjugate building block.

Molecular structure

The X-ray structure of **1** is shown in Fig. 2 together with selected structural parameters. The acetylenic axis is almost linear, and the two axial phenyl groups are staggered by 62.5°
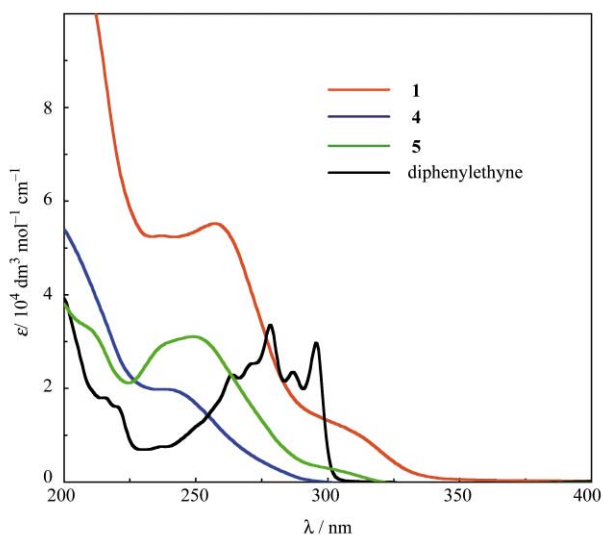

Fig. 1 UV spectra of **1**, **4**, **5**, and diphenylethyne in acetonitrile.

out of the coplanar conformation. The molecular symmetry of **1** is roughly C_2, where the axis of rotation is perpendicular to the acetylenic axis. In each terphenyl unit, the two wing tolyl groups are twisted by 50–58° out of the plane of the axial phenyl group in opposite directions, the two dihedral angles being plus and minus; namely, the symmetry of the terphenyl subunit is nearly C_s rather than C_2 (Scheme 3). X-Ray database analysis was carried out for similar types of *m*-terphenyl substructures: the ratio of C_s type conformations (**6**) and C_2 type ones (**7**) is *ca.* 3 : 1.[19] The conformations are easily influenced by the substituents, the packing energy, and other factors.
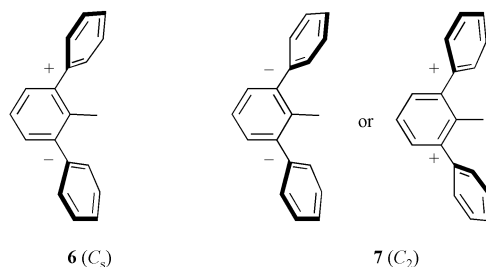
Scheme 3 Possible conformations of terphenyl units. + or − : sign of dihedral angles between the two attaching phenyl groups.

PM3 calculations were performed for **1** to search for other possible conformers: five dihedral angles involving the conformations of the four tolyl groups (ω_{1-4}) and one acetylenic moiety (*a*) were considered to be the variables. As shown in Table 1, five diastereomeric conformers were optimized as energy minima. The global minimum structure takes an approximately D_2 conformation, where the five dihedral angles have the same sign. In the four most stable conformers, the two axial phenyl groups are more twisted, nearly bisected, than those in the X-ray structure. The optimized structure starting from the X-ray structure is the conformer of the fifth lowest energy, being less stable by 8 kJ mol^{-1} than the global minimum. If this energy difference were to reflect the conformational distributions according to the Boltzmann equation, its population would be small. This discrepancy can be explained by the crystal lattice force.

Reactivities of 1

To estimate the effects of the tolyl groups on the reactivities of the triple bonds, **1** was subjected to some reactions typical of ordinary alkynes. Compound **1** was not affected at all by hydrogenation over Pd/C, complexation with Co$_2$(CO)$_8$,[20] and RuCl$_3$-catalyzed oxidation with PhIO,[21] even though the reactions were run under severe conditions. On treatment with Br$_2$,
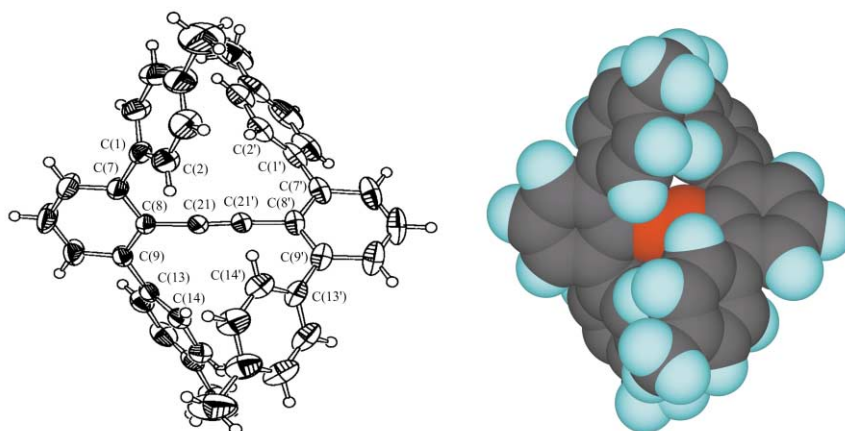

Fig. 2 ORTEP drawing of **1** with 50% thermal probabilities (left) and its CPK presentation (right: sp carbons highlighted in red). Selected structural parameters: C(21)–C(21′) 1.199(2) Å, C(1)–C(7)–C(8) 121.8(1), C(8)–C(9)–C(13) 122.8(1), C(1′)–C(7′)–C(8′) 122.8(1), C(8′)–C(9′)–C(13′) 121.7(1), C(8)–(21)–C(21′) 176.5(2), C(8′)–C(21′)–C(21) 177.6(2), C(2)–C(1)–C(7)–C(8) −58.2(3), C(8)–C(9)–C(13)–C(14) 51.9(2), C(2′)–C(1′)–C(7′)–C(8′) 50.5(3), C(8′)–C(9′)–C(13′)–C(14′) −51.5(3)°.

Table 1 Optimized structures of **1** by PM3 calculations

| Conformer | Dihedral Angles[a]/° | | | | | Relative energy/kJ mol⁻¹ | Approx. symmetry |
	a	ω_1	ω_2	ω_3	ω_4		
1	−84.2	−53.7	−53.7	−53.8	−53.8	0	D_2
2	−88.0	−65.5	−55.3	−55.3	−64.5	2.6	C_2
3	−84.5	69.7	67.2	66.4	68.9	4.8	D_2
4	−87.7	−88.9	62.2	56.1	−56.2	7.4	C_1
5	−63.6	−58.4	59.1	59.1	−58.3	8.1	C_2
X-Ray	−62.5	−58.2	51.9	50.5	−51.5		C_2

[a] a: Dihedral angle between the axial phenyl groups across the acetylenic axis, fixed at negative values. ω_{1-4}: Torsion angles corresponding to C(2)–C(1)–C(7)–(8), C(8)–C(9)–C(13)–C(14), C(2′)–C(1′)–C(7′)–(8′), and C(8′)–C(9′)–C(13′)–C(14′) in the X-ray structure, respectively.

instead of addition to the triple bond, bromination took place slowly at the methyl carbons, presumably *via* a radical pathway. The inertness of **1** can be understood by the CPK model of the X-ray structure in Fig. 2. The cylindrical region of the acetylenic moiety is effectively surrounded by four tolyl groups that prevent reagent molecules from approaching the reaction site.
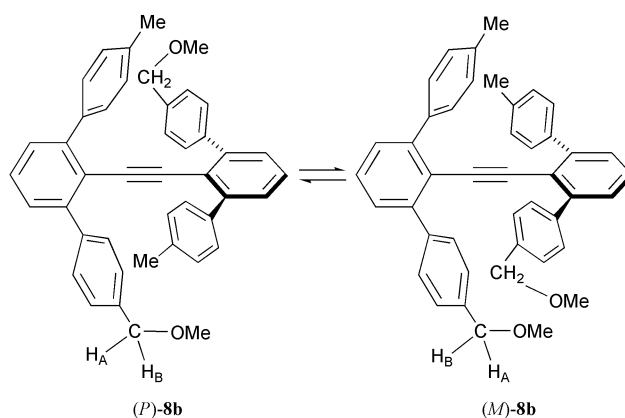
Rotation about acetylenic axis

We cannot obtain kinetic information on the rotation about the acetylenic axis by NMR spectroscopy directly from **1** because of the high symmetry. In order to introduce an NMR probe for observing the dynamic process, **1** was desymmetrized by functionalization of the methyl groups (Scheme 4). The reaction of **1** with a 2.1 molar amount of NBS afforded a mixture of singly and multiply brominated products, from which the bis(bromomethyl) compounds were separated by chromatography as an isomeric mixture (**8a** + **9a**). Subsequent reaction with sodium methoxide afforded ethers **8b** and **9b**, which were separable by chromatography. The structures were unambiguously identified from ¹³C NMR spectra: the numbers of acetylenic and aromatic signals are 1 and 14, respectively, for **8b**, and 2 and 16, respectively, for **9b**. The staggered conformation of **8b** is now chiral (C_2) with a stereogenic axis, and the rotation through the eclipsed form results in enantiomerization accompanied by site exchange of the diastereotopic methylene protons (Scheme 5). Variable temperature ¹H NMR measurements revealed that the signal due to the methylene protons was observed as a sharp singlet at room temperature and even at −100 °C in CD₂Cl₂, THF-d_8, or toluene-d_8.[22] This finding means that the site exchange, namely, enantiomerization by the axial rotation, takes place much faster than the NMR time scale at −100 °C, the upper limit of the barrier to rotation being 35 kJ mol⁻¹.
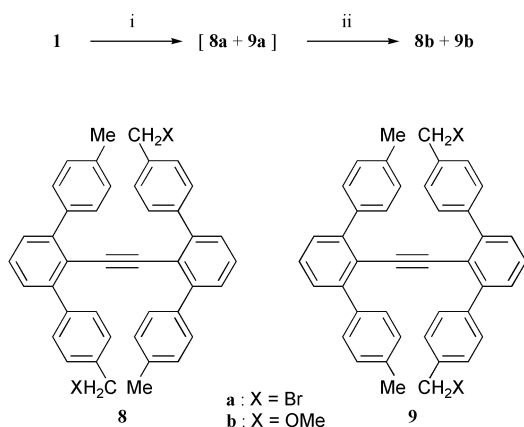
Scheme 4 *Reagents and conditions:* i. NBS, (PhCOO)₂, CCl₄, then separation from other brominated products; ii. MeONa, MeOH, then separation.

In a rigid molecular model of **8b** or **1**, the wing tolyl groups interact strongly in the transition state of the rotation, where the two axial phenyl groups are nearly coplanar. Nevertheless,

Scheme 5 Enantiomerization *via* rotation about the acetylenic axis in **8b**.

the rotation takes place rapidly in real molecules, this meaning that the steric interactions in the transition state are significantly relieved by the structural deformations. The bending deformation of the C–C≡C–C moiety plays an important role in avoiding excess steric interactions, as was observed for the rotational isomerism in the bis(9-triptycyl)ethyne system.[1,7] Moreover, the flexibility of the tolyl groups can decrease the steric interactions in the transition state by correlated rotation, such as that of a gear, and by bending deformation, such as the flapping of wings. This result indicates that not only the steric size of the substituents but also their rigidity is a key factor in effectively enhancing the rotational barrier in diarylethynes.

As for cyclic diarylalkynes, a high barrier of more than 80 kJ mol⁻¹ was observed for a cyclic turnstile-like molecule, where the central spindle moiety was conformationally locked by the steric interactions with the macrocyclic framework.[11] To realize such a high barrier in acyclic alkynes, the molecules should meet structural requirements higher than those of cyclic alkynes. In line with this strategy, we are investigating more rigid systems, *e.g.*, ethynes with 1-naphthyl or 9-anthryl groups.

Experimental

General

Melting points are uncorrected. ¹H and ¹³C NMR spectra were measured on a Varian Gemini-300 spectrometer at 300 and 75 MHz, respectively, unless otherwise mentioned. Some ¹³C NMR spectra were measured on a JEOL Lambda 500 spectrometer at 125 MHz. High-resolution mass spectra were measured on a JEOL MStation-700 spectrometer by the FAB method. Elemental analyses were performed by a Perkin-Elmer 2400 series analyzer. UV spectra were measured with a Hitachi U-3000 spectrometer with a 10 mm cell. 2′-Iodo-4,4″-dimethyl-1,1′;3′,1″-terphenyl **4** was prepared by the Hart reaction of 1,3-dichloro-2-iodobenzene and *p*-methylphenylmagnesium bromide followed by the treatment with I₂.[13,14] UV data of **4**: λ_{max}(CH₃CN)/nm 238 (ε/dm³ mol⁻¹ cm⁻¹ 20000).

Bis(4,4″-dimethyl-1,1′;3′,1″-terphenyl-2′-yl)ethyne (1)

A solution of **4** (77 mg, 0.20 mmol) in 10 cm³ of 1,4-dioxane was degassed by bubbling argon gas for 30 min, to which bis-(tributylstannyl)ethyne (69 mm³, 0.13 mmol), lithium chloride (25 mg, 0.58 mmol), and Pd(PPh₃)₄ (11.5 mg, 0.010 mmol) were added. The mixture was heated under reflux in an atmosphere of argon for 4 days. The solvent was removed by evaporation, and the residue was subjected to column chromatography on silica gel using hexane–dichloromethane (10 : 1) as eluent. Recrystallization from hexane–dichloromethane gave **1** (34 mg, 63%) as colorless crystals; mp 225–227 °C (Found: C, 93.17; H, 6.45. $C_{42}H_{34}$ requires C, 93.57; H, 6.43%); λ_{max}(CH₃CN)/nm 258 (ε/dm³ mol⁻¹ cm⁻¹ 55000), *ca.* 310 (12000, sh); δ_H (CDCl₃) 2.34 (12H, s, Me), 7.06–7.32 (22H, m, Ph); δ_C (CDCl₃) 21.3 (Me), 93.8 (C≡C), 120.1, 127.6, 128.2, 128.5, 129.3, 136.8, 138.2, 144.9; *m/z* 539.2767 (FAB, MH⁺), calc. for $C_{42}H_{34}$ 539.2739 (MH).

2′-Ethynyl-4,4″-dimethyl-1,1′;3′,1″-terphenyl (5)

To a degassed mixture of 40 cm³ of triethylamine and 20 cm³ of 1,4-dioxane were added **4** (2.00 g, 5.20 mmol), Pd(PPh₃)₂Cl₂ (195 mg, 0.26 mmol), triphenylphosphine (136 mg, 0.52 mmol), copper(I) iodide (20 mg, 0.10 mmol), and (trimethylsilyl)ethyne (6.0 cm³, 10 mmol). The mixture was heated under reflux in an atmosphere of argon for 12 h. The volatile materials were removed by evaporation, and the crude material was purified by column chromatography on silica gel using hexane–dichloromethane (50 : 1) as eluent to give 4,4″-dimethyl-2′-[(trimethylsilyl)ethynyl]-1,1′;3′,1″-terphenyl (1.27 g, 69%) as yellow oil; δ_H (CDCl₃) −0.05 (9H, s, TMS), 2.41 (6H, s, Me), 7.19–7.41 (8H, m, Ph), 7.50–7.54 (3H, m, Ph); δ_C (CDCl₃) −0.3 (SiMe₃), 85.9 (C≡C), 88.1 (C≡C), 120.1, 127.3, 127.6, 128.3, 129.6, 140.8, 145.4; *m/z* (FAB, MH⁺) 355.1915, calc. for $C_{23}H_{26}Si$ 355.1882 (MH). This coupling product (1.27 g, 3.59 mmol) was dissolved in 20 cm³ of tetrahydrofuran. To the solution was added 4.0 cm³ (4.0 mmol) of 1.0 mol dm⁻³ solution of tetrabutylammonium fluoride in tetrahydrofuran. After stirring for 2 h at room temperature, this mixture was treated with *ca.* 5 cm³ of water. Most of the solvent was removed by evaporation, and the residue was extracted with dichloromethane. The extract was washed with brine, dried over magnesium sulfate, and evaporated under reduced pressure. The crude material was purified by column chromatography on silica gel using hexane–dichloromethane (10 : 1) as eluent. Recrystallization from hexane–dichloromethane gave **5** (99 mg, 97%) as colorless crystals; mp 116–118 °C (Found: C, 93.27; H, 6.45. $C_{22}H_{18}$ requires C, 93.57; H, 6.43%); λ_{max}(CH₃CN)/nm 249 (ε/dm³ mol⁻¹ cm⁻¹ 31000), *ca.* 300 (3000, sh); δ_H (CDCl₃) 2.41 (6H, s, Me), 2.96 (1H, s, C≡C–H), 7.23–7.52 (11H, m, Ph); δ_C (CDCl₃) 21.25 (Me), 82.20 (C≡C), 83.92 (C≡C), 111.52, 118.87, 128.38, 128.56, 129.35, 137.15, 137.96, 145.80.

Synthesis of 1 by Sonogashira coupling

A solution of **4** (680 mg, 1.77 mmol) and **5** (500 mg, 1.77 mmol) in a mixture of 10 cm³ of triethylamine and 5 cm³ of 1,4-dioxane was degassed similarly to that above. To the solution were added Pd(PPh₃)₂Cl₂ (66 mg, 0.089 mmol), copper(I) iodide (6.7 mg, 0.035 mmol), and triphenylphosphine (50.6 mg, 0.177 mmol). The mixture was heated under reflux in an atmosphere of argon for 12 h. The volatile materials were removed by evaporation. The crude extract was separated by column chromatography on silica gel using hexane–dichloromethane (10 : 1) as eluent to give **1** (210 mg, 44%) and the butadiyne (40 mg, 8%) with a recovery of 20% of **4**. The structure of the by-product was confirmed by independent synthesis, namely, coupling of **5** with copper(II) acetate in pyridine. An analytical sample of 1,4-bis(4,4″-dimethyl-1,1′;3′,1″-terphenyl-2′-yl)-1,3-butadiyne was obtained by recrystallization from hexane–dichloromethane as colorless crystals; mp 171–172 °C (Found: C, 94.05; H, 6.05. $C_{44}H_{34}$ requires C, 93.91; H, 6.09%); δ_H (CDCl₃) 2.34 (12H, s, Me), 7.06–7.32 (22H, m, Ph); δ_C (CDCl₃) 21.3 (Me), 80.7 (C≡C), 81.3 (C≡C), 118.7, 128.3, 128.5, 128.6, 129.3, 137.0, 137.5, 146.1; *m/z* 563.2770 (FAB, MH⁺), calc. for $C_{44}H_{34}$ 563.2739 (MH).

Reactions of 1

Bromination. To a solution of **1** (50 mg, 0.094 mmol) in 10 cm³ of tetrachloromethane in a flask covered by aluminum foil was added 0.20 mmol of bromine in tetrachloromethane. The mixture was stirred for 2 h at room temperature, and then heated at 60 °C for 30 h. The solvent was evaporated and the residue was analyzed by TLC and ¹H NMR. The product distributions were 68%, 25%, and 7% for the starting material, the mono(bromomethyl) compound, and the bis(bromomethyl) compound (mixture of isomers), respectively. The brominated products were identical to those formed by the NBS bromination described later.

Hydrogenation. A solution of **1** (50 mg, 0.094 mmol) in 3 cm³ of ethyl acetate was stirred overnight in the presence of 10 mg of Pd/C under an atmosphere of hydrogen at ambient pressure. Diphenylethyne was completely reduced into 1,2-diphenylethane under the same conditions. Even though the reaction mixture of **1** was further stirred at 60 °C for 22 h, only the starting material was recovered. Complexation with dicobalt hexacarbonyl[20] and ruthenium(III) chloride catalyzed oxidation[21] were carried out by the methods described in the literature; however, no significant reactions were observed

NBS bromination of 1

A suspension of **1** (432 mg, 0.80 mmol), *N*-bromosuccinimide (300 mg, 1.68 mmol), and benzoyl peroxide (30 mg, 0.12 mmol) in 10 cm³ of tetrachloromethane was heated under reflux for 4 h. After insoluble materials were removed by filtration, the solvent was removed by evaporation. The products were separated by column chromatography on silica gel using hexane–dichloromethane (2 : 1) as eluent. The starting material, monobromide, dibromide, and tribromide were eluted in this order. The dibromide was obtained as a mixture of two isomers (**8a** and **9a**), which were inseparable and used in the next reaction without isolation. A mixture of bis(4-bromomethyl-4″-methyl-1,1′;3′,1″-terphenyl-2′-yl)ethyne **8a** and [4,4″-bis(bromomethyl)-1,1′;3′,1″-terphenyl-2′-yl](4,4″-dimethyl-1,1′;3′,1″-terphenyl-2′-yl)ethyne **9a**: total yield 40%; δ_H (CDCl₃) 2.36 (6H, s, Me), 4.51 (4H, s, –CH₂Br), 7.08–7.31 (22H, m, Ph); *m/z* 697.0939 (FAB, MH⁺), calcd for $C_{42}H_{32}{}^{79}Br^{81}Br$ 697.0933 (MH). Analytical and spectroscopic data of other products: (4-bromomethyl-4″-methyl-1,1′;3′,1″-terphenyl-2′-yl)(4,4″-dimethyl-1,1′;3′,1″-terphenyl-2′-yl)ethyne: yield 25%; mp 224–226 °C; δ_H (CDCl₃) 2.34 (9H, s, Me), 4.51 (2H, s, –CH₂Br), 7.05–7.31 (22H, m, Ph); *m/z* 617.1803 (FAB, MH⁺), calcd for $C_{42}H_{33}{}^{79}Br$ 617.1844 (MH). [4,4″-bis(bromomethyl)-1,1′;3′,1″-terphenyl-2′-yl](4-bromomethyl-4″-methyl-1,1′;3′,1″-terphenyl-2′-yl)ethyne: yield 17%; mp 224–227 °C; δ_H (CDCl₃) 2.34 (3H, s, Me), 4.51 (6H, s, –CH₂Br), 7.06–7.32 (22H, m, Ph); *m/z* 775.0010 (FAB, MH⁺), calcd for $C_{42}H_{31}{}^{79}Br_2{}^{81}Br$ 775.0037 (MH).

Bis[4-(methoxymethyl)-4″-methyl-1,1′;3′,1″-terphenyl-2′-yl]ethyne (8b)

A mixture of **8a** and **9a** (75 mg, 0.11 mmol) was added to a solution of sodium methoxide (24 mg, 0.44 mmol) in 3 cm³ of methanol. The mixture was heated under reflux for 2 h, after which time it was treated with water (*ca.* 10 cm³) and dichloromethane (*ca.* 10 cm³). The organic layer was separated, dried over magnesium sulfate, and evaporated. The isomers were

separated by column chromatography on silica gel with hexane–dichloromethane (1 : 1) as eluent. The easily and less easily eluted isomers were assignable to **8b** and **9b**, respectively, from the signal patterns of ^{13}C NMR. **8b**: mp 163.0–164.0 °C; δ_H (CDCl$_3$) 2.34 (6H, s, Me), 3.38 (6H, s, OMe), 4.45 (4H, s, CH$_2$), 7.06 (4H, d, J 7.9 Hz, Ph), 7.15 (4H, d, J 7.9 Hz, Ph), 7.18–7.31 (14H, m, Ph); δ_C (125 MHz; CDCl$_3$) 21.3 (Me), 58.2 (OMe), 74.5(CH$_2$), 93.8 (C≡C), 120.1, 127.1, 127.7, 128.2, 128.4, 128.5, 129.3, 129.5, 136.9, 137.1, 138.1, 140.5, 144.7, 145.0; m/z 599.2997 (FAB, MH$^+$), calcd for C$_{44}$H$_{38}$O$_2$ 599.2950 (MH). The variable temperature ^{1}H NMR spectra of **8b** were measured on a Bruker AMX-400 spectrometer at 400 MHz in CD$_2$Cl$_2$, THF-d_8, or toluene-d_8. The observed temperature was calibrated from the chemical shift difference of methanol signals. No significant broadening was observed for the signal due to the methylene protons at −100 °C. The upper limit of the rotational barrier was 35 kJ mol^{-1}, assuming that the rate of rotation was >100 s^{-1} at that temperature. [4,4″-Bis(methoxymethyl)-1,1′;3′,1″-terphenyl-2′-yl](4,4″-dimethyl-1,1′;3′,1″-terphenyl-2′-yl)ethyne (**9b**): mp 135.5–136.5 °C; δ_H (CDCl$_3$) 2.34 (6H, s, Me), 3.38 (6H, s, OMe), 4.46 (4H, s, CH$_2$O), 7.07 (4H, d, J 7.9 Hz, Ph), 7.17 (4H, d, J 7.9 Hz, Ph), 7.18–7.33 (14H, m, Ph); δ_C (125 MHz; CDCl$_3$) 21.3 (Me), 58.2 (OMe), 74.5 (CH$_2$), 93.4 (C≡C), 94.1 (C≡C), 120.0, 120.2, 127.1, 127.7, 127.7, 128.2, 128.4, 128.5, 129.3, 129.5, 136.8, 137.1, 138.2, 140.4, 144.7, 144.9; m/z 599.2997 (FAB, MH$^+$), calcd for C$_{44}$H$_{38}$O$_2$ 599.2950 (MH).

Crystal data of 1 ‡

Data were collected on a Rigaku RAXIS-IV imaging plate diffractometer. All intensity measurements were performed using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). A single crystal of **1** suitable for X-ray diffraction was recrystallized from hexane–dichloromethane, C$_{42}$H$_{34}$, $M = 538.73$, monoclinic, $a = 10.5516(6)$, $b = 26.343(2)$, $c = 11.8322(9)$ Å, $\beta = 101.243(5)°$, $V = 3225.7(4)$ Å^3, $T = 213$ K, space group $P2_1/n$ (no. 14), $Z = 4$, $\rho_{calcd} = 1.109$ g cm^{-3}, $\mu = 0.62$ cm^{-1}, 10208 reflections measured, 6120 unique that were used in all calculations. The final $R_1(F) = 0.0530$ (for 4149 reflections with $F_o{}^2 > 2\sigma(F_o{}^2)$), w$R_2(F^2) = 0.1520$ for all unique reflections. CCDC reference number 205343.

PM3 calculations

The calculations of **1** were performed using the MOPAC 2000 program on a personal computer. The structures were optimized from the X-ray structure and other various conformations. The CPK presentation in Fig. 2 was generated by the Chem3D pro version 5.0 program.

‡ CCDC reference number205343. See http://www.rsc.org/suppdata/ob/b3/b302016a/ for crystallographic data in .cif or other electronic format.

Acknowledgements

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