

Biphenyl-Based Disc- vs. Rod-Shaped Phenylacetylenes: Mesomorphism and Electronic Properties

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Keywords: Liquid crystals / Structure-activity relationships / Alkynes / Cross-coupling / Biphenyls

A standard Sonogashira coupling protocol has been applied for the preparation of a C_3 -symmetric phenylacetylene (**2**) and the corresponding linear phenylacetylene (**3**) incorporating terminal biphenyl substituents. The study of the mesomorphic properties of the target compounds, as well as mixtures of both, reveals that only the calamitic biphenylacetylene **3** forms smectic liquid crystals. Upon investigating the

electronic situation of both biphenylacetylenes by spectroscopic methods and computational calculations, it becomes evident that **2** can be considered the trimeric analogue of **3** which however does not form liquid crystalline phases.

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Introduction

The enormous advance which the field of liquid crystals (LCs) has experienced during the past three decades is a direct consequence of the application of predominantly nematic LCs in display technology. The underlying physical phenomena consist in the ability of liquid-crystalline materials to rotate plane-polarized light (birefringence), which can be electrically switched by reorienting the calamitic mesogens in an electric field.^[1] Smectic LCs are typically rod-like molecules composed of an elongated rigid core with flexible side chains.^[2] Aside from smectic LCs, formed by rigid-rod mesogens such as biphenyl derivatives as a prime example, the construction of columnar LCs based on disk-shaped mesogens has attracted increasing attention, lately. Again, their potential technical application in electro-optical devices has been the driving force to press forward this relatively young research area.^[3] Here, one of the most attractive features is the one-dimensional electronic conductance along the axis perpendicular to the columnar stacks, typically formed by discotic molecules with extended π -systems.^[4] Examples of discotic mesogens with electro-optical activity include aromatic and heteroaromatic polycyclic and

macrocyclic compounds,^[5] but also more simple π -extended (hetero)benzenes and self-assembled systems.^[6] The factors controlling the self-assembly of columnar LCs are governed by weak interactions such as π -stacking, van der Waals and dispersion forces, dipolar interactions and others.^[7] A recent study by Williams et al. has stressed the importance of electrostatic contributions in usually highly polar or polarizable systems.^[8] We have recently demonstrated the possibility to obtain functional, bulk-phase devices from pre-functionalized benzene-based, low-molecular-weight building units forming liquid crystals, directed towards nonlinear optical and opto-electronic applications.^[9] As an intermediate between the discotic and calamitic mesogens, disc-rod-shaped mesogens have raised considerable interest over the last few years, and the resulting LC phases have been studied extensively. Mesogenic structures of this type are commonly designed by connecting rod-like subunits to a discotic central platform, for example benzene or triphenylene.^[10] The search for a (theoretically predicted) biaxial nematic phase, as well as the uncommon miscibility of rod-like with disc-shaped molecules in the LC phase has pushed the limits in this recent field of LC research.^[11]

Results and Discussion

In the present contribution we wish to report the synthesis of biphenylacetylene-based linear and disc-rod-shaped molecules and establish a relationship between the molecular and electronic structure, and their mesomorphic behavior. Acetylenic scaffolding has gained increasing importance for the construction of functional opto-electronic materials.^[12] The conjugation pathway in phenylacetylene systems is governed by the symmetry and directionality of the car-

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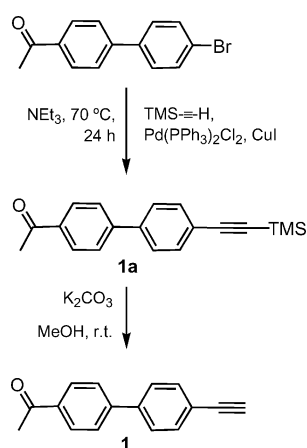
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bon-carbon triple bond, thus it can be considered as strictly one-dimensional (linear) and free from conformational complications arising from the presence of energetically relevant (*cis/trans* or rotational) isomers.^[13]

Synthesis

We have chosen the Sonogashira cross-coupling reaction as the method of choice to prepare the respective phenylethyne compounds in a straight forward, target-oriented approach.^[14] The biphenyl-substituted acetylene **1** is obtained in two steps from commercially available 4'-(4-bromophenyl)acetophenone in good yields, and is used as the free acetylene compound in the following coupling reactions (Scheme 1).



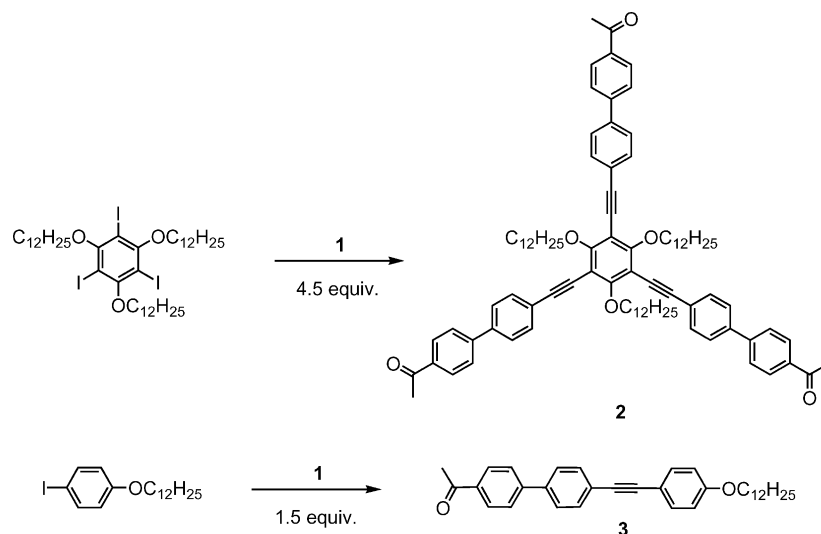
Scheme 1. Synthesis of the biphenylacetylene **1**.

In the syntheses of the 1,3,5-tris(alkynyl)benzene **2**, starting from 1,3,5-triiodo-2,4,6-tris(dodecyloxy)benzene,^[9] and the linear reference compound **3**, obtained from 1-iodo-4-dodecyloxybenzene, a 1.5-fold excess of **1** with respect to the iodo functions in the starting aryl compound has been

employed (Scheme 2). In all coupling steps, the Pd⁰/Cu^I catalyst system is utilized in a 2.5 mol-% quantity per aryl halide. In both cases, the reaction mixtures were heated at 70 °C for 18 h in a toluene/triethylamine mixture (1:1). While **3** is obtained in 67% yield without optimizing the reaction conditions, a low yield of 19% for the threefold coupling product **2** reflects the unfavorable electronic and steric conditions of the triiodo starting material brought about by the bulky, electron-rich alkoxy side-chains.

Electronic Structure

The optical transitions can be tuned conveniently by adjusting the substitution pattern of the phenyl subunits. Both **2** and **3** are conjugated donor- π -acceptor systems with an octopolar or dipolar character, respectively, where the alkoxy substituents act as donor groups and the acetyl moiety as electron-withdrawing function.^[15] The type of the LC phase formed should primarily depend on the molecular structure of the constituting mesogens: Compound **3** represents the typical elongated rigid-rod like mesogen, while **2** is a π -extended, disc-shaped molecule with C_3 -symmetry. Formally, **2** can also be considered as a trimer of **3**, being composed of three linear biphenylacetylene subunits connected to a central benzene core. In order to assess the electronic nature of the target compounds, the UV/Vis absorption and fluorescence spectra of **2** and **3** have been recorded in solution. Spectroscopically, compound **2** behaves as a trimeric assembly of **3** in which the three biphenylacetylene fragments are electronically isolated and the electronic transitions are located in the linear fragments.^[16] The long-wavelength charge-transfer absorption band is situated roughly at the same position for both **2** [334 nm, $\log(\epsilon_{334}) = 5.084$] and **3** [329 nm, $\log(\epsilon_{329}) = 4.533$]; the bathochromic displacement of 5 nm is negligible. The molecular absorptivity for the trigonal **2** amounts approximately to the threefold value (3.52) compared to the linear biphenylacetylene



Scheme 2. Synthesis of the 1,3,5-tris(alkynyl)benzene **2** and the linear phenylacetylene **3**.

3. Further evidence for the distinctive electronic situation in both push-pull systems is obtained from computational calculations which reveal a substantial dipole moment of 3.47 D for **3**.^[17] In contrast, **2** exhibits a pronounced octopolar character as manifested by the tensor elements in the molecule plain (i.e. the *x*- and *y*-direction) contributing to the overall polarization of **2** (Table 1).^[18]

Table 1. Calculated polarization (field-independent basis Deye-Ang**2).

β -Components					
XXX	5.44	YYY	-324.51	ZZZ	1.68
XXY	808.79	YYZ	237.37	YZZ	2.69
XXZ	-486.09	YYX	14.95	XZZ	57.94
		XYZ	383.56		

Both compounds are well fluorescent with quantum yields $\Phi_{\text{Fl}}(\mathbf{2}) = 0.26$, and $\Phi_{\text{Fl}}(\mathbf{3}) = 0.12$, respectively.^[19] Again, the fluorescence emission maxima are located in the same wavelength region [**2**: λ_{max} (em) = 446 nm; **3**: λ_{max} (em) = 435 nm]. The large Stokes shifts > 100 nm are attributed to the structural changes (planarization) occurring in the biphenyl subunits upon excitation (Figure 1).^[20]

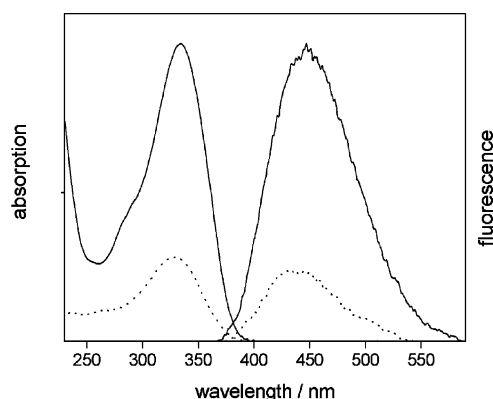


Figure 1. UV/Vis absorption and fluorescence spectra of **2** (—) and **3** (···) in CH_2Cl_2 solution, $c = 10^{-6} \text{ mol L}^{-1}$, normalized to the absorption and emission maximum of **2**.

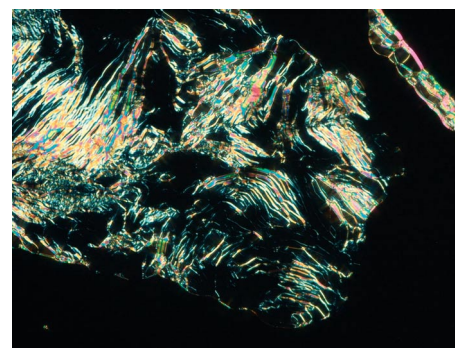
Liquid Crystal Properties

The mesomorphic properties of **2** and **3** have been studied by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). Transition temperatures and their associated enthalpy changes in the second heating cycle recorded at 10 °C/min are gathered in Table 2.

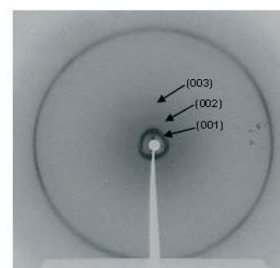
Table 2. Optical and thermal properties of **2** and **3**.

Phase ^[a]		$T^{\text{[b]}}/\text{°C}$		$(\Delta H / \text{kJ mol}^{-1})$	
2	Cr	144 (9.1)	Cr'	168 (36.2)	I
3	Cr	101 (32.0)	Cr'	194 (2.9)	SmA
					211 (4.1) I

Compound **3** shows two crystalline phases and a high-temperature SmA mesophase which is identified from the homeotropic texture (Figure 2, a). To confirm the type of mesophase, X-ray diffraction experiments were performed and the patterns obtained present a diffuse halo corresponding to a mean distance of 4.4 Å. This feature is characteristic of the liquid-like order of the aliphatic chains in a liquid-crystal phase. A set of sharp maxima in the low-angle region with a reciprocal spacing ratio of 1:2:3 is also observed (Figure 2, b). This maxima can be assigned to the (001), (002) and (003) reflections of a lamellar arrangement. The maxima provide a layer spacing of 36.5 Å for this mesophase which corresponds to the estimated molecular length.



(a)



(b)

Figure 2. a) Microphotograph of **3** observed by POM of SmA phase at 202 °C. b) XRD pattern of SmA phase.

In contrast to the mesomorphic behavior of the rod-shaped derivative **3**, the discotic biphenyl-substituted acetylene **2** does not display LC properties. It directly melts from the crystal at 168 °C. In order to probe the miscibility of both compounds, and in order to induce liquid crystallinity in **2**, different mixtures of **2** and the calamitic **3** have been prepared at mol ratios of 1:1, 1:2, and 1:3. However, in all three cases the mixtures behave as two separate compounds with the crystalline **2** simply acting as “impurity” in the smectic LC phase formed by **3**.

Conclusions

In conclusion, we have described the synthesis of a rigid, extended trigonal biphenyl-substituted acetylene **2** and its

linear analogue **3** by Sonogashira coupling of the respective aryl iodides with the biphenyl-substituted acetylene **1**, which itself constitutes a versatile building block for the preparation of extended π -systems. Both target compounds display attractive spectroscopic properties as a consequence of the donor-acceptor substitution pattern, being of an octopolar nature in the case of **2** and dipolar for the linear **3**. While the calamitic alkyne **3** displays interesting mesomorphic properties, the disc-rod-shaped **3** does not form a LC phase; neither do mixtures of both **2** and **3**. However, it is reasonable to assume that the preparation of analogues of **2** with advanced LC properties can be achieved in a straightforward manner by simply replacing the linear C_{12} alkoxy side chains by longer, branched, or fluorinated ones,^[21] and thereby counteract the non-covalent (stacking) interactions with favor crystallization of the extended π -system.

Experimental Section

General: All solvents and reagents were purchased from Aldrich and used without further purification. Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected. 1H and ^{13}C NMR spectra were recorded with a Bruker AC-300 and spectrometer in deuterated chloroform (deuteration grade >99.80%) with the solvent signal serving as internal standard. Mass spectra (MALDI, EI) were recorded with a HP1100MSD spectrometer. Elemental analyses were performed with a LECO CHNS 932 micro-analyzer. Spectroscopic measurements were performed using HPLC-quality solvents, and are solvent corrected. UV/Vis spectra were measured with a HP 8453 (Hewlett–Packard) spectrophotometer. A Perkin–Elmer LS50B luminescence spectrometer was employed for the fluorescence studies, in a four-sided quartz cell at room temperature in a right-angle geometry and are corrected for the spectral response for the detection system. Mesophase analysis was performed using a Linkam THMS600 hot stage and an Olympus polarizing microscope equipped with an Olympus DP12 digital camera. Transition temperatures and enthalpies were obtained by differential scanning calorimetry with a DSC-MDSC TA Instruments Q-1000 apparatus at heating and cooling rates of 10 °C/min. The apparatus was previously calibrated with indium (156.6 °C, 28.44 J/g). Powder X-ray diffraction patterns were obtained using a pinhole camera (Anton Paar) operating with a point-focused Ni-filtered $Cu-K_{\alpha}$ beam. The sample was held in Lindemann glass capillaries (0.9 and 1 mm diameter) and heated, when necessary, with a variable-temperature attachment. The diffraction patterns were collected on flat photographic film.

Computational Methods: Compounds **2** and **3** were evaluated with Gaussain 03 and its suite of algorithms. Both compounds geometries were optimized using HF 32–1 G, followed by a frequency calculation to determine the zero point energy. For the purposes of understanding the behavior of the octopolar compound, **2**, this was deemed a sufficient level of theory for understanding its electro-optical properties.

Materials

4'-(4-(Trimethylsilyl)ethynyl)phenyl)acetophenone (1a): 4'-(4-Bromophenyl)acetophenone (690 mg, 2.5 mmol) was heated together with $Pd(PPh_3)_2Cl_2$ (44 mg, 0.063 mmol), CuI (12 mg, 0.063 mmol), and trimethylsilylacetylene (0.7 mL, 5.0 mmol) in NEt_3 (15 mL) at 70 °C for 18 h in a pressure tube. The solvent was removed in

vacuo, the remaining solid was suspended in water (20 mL) and extracted with $EtOAc$ (3×20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated to dryness to leave a solid which was purified by column chromatography (hexane/ $EtOAc$, 10:1) and final recrystallization from $EtOH$, yielding pure **1a** as colorless plates. Yield 621 mg, 85%; m.p. 138 °C. 1H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d_{AB} , J = 8.4 Hz, 2 H), 7.67 (d_{AB} , J = 8.6 Hz, 2 H), 7.56 (s, 4 H), 2.63 (s, 3 H), 0.27 (s, 9 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.5, 144.6, 139.6, 136.0, 132.4, 128.9, 127.0, 126.9, 123.0, 104.6, 95.6, 26.6, –0.1 ppm. $C_{19}H_{20}OSi$ (292): calcd. C 78.08, H 6.85; found C 77.63, H 6.86.

4'-(4-Ethynylphenyl)acetophenone (1): Compound **1a** (584 mg, 2.0 mmol) was stirred with K_2CO_3 (560 mg, 4.0 mmol) in $MeOH$ (20 mL) at room temp. for 5 h. The solvent was removed in vacuo, the remaining solid was suspended in water (20 mL) and extracted with $EtOAc$ (3×10 mL). The combined organic phases were dried ($MgSO_4$) and concentrated to dryness to leave a colorless solid which was recrystallized from $EtOH$ to give pure **1** as colourless crystals. Yield 357 mg, 81%; m.p. 164 °C. 1H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d_{AB} , J = 8.4 Hz, 2 H), 7.67 (d_{AB} , J = 8.6 Hz, 2 H), 7.59 (s, 4 H) 3.16 (s, 1 H), 2.64 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.6, 144.7, 140.1, 136.2, 132.7, 128.9, 127.1, 127.0, 122.0, 83.2, 78.4, 26.6 ppm. $C_{16}H_{12}O$ (220): calcd. C 87.25, H 5.49; found C 87.85, H 5.63.

1,3,5-Tris[4'-(4-acetylphenyl)phenylethynyl]-2,4,6-tris(dodecyloxy)-benzene (2): 1,3,5-Triiodo-2,4,6-tris(dodecyloxy)benzene (502 mg, 0.5 mmol) and **1** (495 mg, 2.25 mmol) were heated together with $Pd(PPh_3)_2Cl_2$ (27 mg, 0.038 mmol), CuI (7 mg, 0.056 mmol), in toluene/ NEt_3 (1:1, 15 mL) at 70 °C for 18 h. After aqueous and chromatographic (hexane/ $EtOAc$, 5:1) workup and final recrystallization from diethylketone, **2** was obtained as colourless solid in 19% yield (122 mg). 1H NMR (300 MHz, $CDCl_3$): δ = 8.06 (d_{AB} , J = 8.2 Hz, 6 H), 7.71 (d_{AB} , J = 8.2 Hz, 6 H), 7.64 (s, 12 H), 4.40 (t, J = 6.1 Hz, 6 H), 2.65 (s, 9 H), 1.91 (q, J = 7.0 Hz, 6 H), 1.62 (q, J = 7.8 Hz, 6 H), 1.56–1.12 (m, 48 H) 0.84 (t, J = 6.5 Hz, 9 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.5, 163.1, 144.7, 139.5, 136.0, 131.8, 129.0, 127.2, 127.0, 123.5, 108.2, 96.7, 82.9, 74.9, 31.9, 30.6, 29.7 (4), 29.6 (9), 29.4 (4), 29.3 (5), 26.6, 26.4, 22.6, 14.1 (one alkyl ^{13}C signal missing) ppm. $C_{90}H_{108}O_6 \cdot H_2O$ (1286): calcd. C 82.91, H 8.50; found C 82.87, H 8.43.

[4'-(4-Acetylphenyl)phenylethynyl]-4-dodecyloxybenzene (3): 4-Iodo-(dodecyloxy)benzene^[22] (280 mg, 0.5 mmol) and **1** (165 mg, 0.75 mmol) were treated and purified under the same conditions as for **2** to give pure **3** as pale yellow solid after final recrystallization from $EtOH$ in 67% yield (161 mg). 1H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d_{AB} , J = 8.2 Hz, 2 H), 7.70 (d_{AB} , J = 8.2 Hz, 2 H), 7.60 (s, 4 H), 7.48 (d_{AB} , J = 8.8 Hz, 2 H), 6.88 (d_{AB} , J = 8.8 Hz, 2 H), 3.98 (t, J = 6.5 Hz, 2 H), 2.64 (s, 3 H), 1.79 (q, J = 5.5 Hz, 2 H), 1.48–1.27 (m, 18 H) 0.88 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.7, 159.4, 144.9, 139.1, 136.0, 133.1, 132.0, 129.0, 127.3, 127.1, 127.0, 123.7, 114.6, 90.9, 87.6, 68.1, 31.9, 29.6 (4), 29.6 (2), 29.5 (8), 29.4, 29.3, 29.2, 26.7, 26.0, 22.7, 14.1 ppm. $C_{34}H_{40}O_2$ (480): calcd. C 84.96, H 8.39; found C 84.79, H 8.30.

Acknowledgments

This work was supported by the Spanish Ministerio de Ciencia y Tecnología (MCYT) (grants CTQ2007-65683, MAT 2006-13571-CO2-01), and the Comunidad Autónoma de Madrid / UAM (grant CCG06-UAM/MAT-0449).

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Received: June 11, 2008

Published Online: August 14, 2008