Macroscopic Helical and Cylindrical Morphologies from Achiral 1,3-Diynes

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Diacetylenes containing an anhydride function (**1**) or two *s*-triazine groups (**2**) precipitate from organic solvents in large helical or cylindrical forms, respectively, which have been studied by optical and scanning electron microscopy. X-ray diffraction studies on helices of 10,12-tricosadynoic anhydride, $\{n\text{-}C_{10}H_{21}C{\equiv}C{-}C{\equiv}C(CH_2)_8CO\}_2O$ (**1**), show a lamellar crystalline phase with layer spacing of 42.5 ± 0.5 Å and support a noninterdigitated bilayer structure. The crystal structure of a related amphiphilic diacetylene, $n\text{-}C_{10}H_{21}C{\equiv}C{-}C{\equiv}C(CH_2)_8CH_2OSO_2C_6H_4Me\text{-}4$ (**3**), is also reported and discussed: triclinic, $P\bar{1}$, $a = 5.9730(10)$ Å, $b = 8.0690(10)$ Å, $c = 29.524(3)$ Å; $\alpha = 95.020(10)°$, $\beta = 93.260(10)°$, $\gamma = 97.480(10)°$. The nonamphiphilic, α,ω-difunctionalized diacetylene, 6,6′-(deca-4,6-diyne-1,10-diyl)di-2,4-diamino-1,3,5-triazine, $2\text{-}\{4,6\text{-}(NH_2)_2C_3N_3\}(CH_2)_3C{\equiv}C{-}C{\equiv}C(CH_2)_3\text{-}\{C_3N_3(NH_2)_2\text{-}4,6\}\text{-}2$ (**2**), forms solid cylindrical particles of mean length ∼0.5 mm, which may derive from helix formation. The origin of macroscopic chirality in the solid-state morphology of the achiral anhydride (**1**) is discussed.

Introduction

Considerable effort has been expended on the synthesis of amphiphilic 1,3-diynes and on investigations of their unusual microstructures formed through self-assembly.[1] Prototype compounds are hydrated chiral diacetylenic phosphatidylcholines which generally result in the formation of tubules and helices;[2] other amphiphiles forming similar morphologies include chiral diacetylenic aldonamides.[3] The factors governing self-assembly are complex, and while chirality in the substrate can play a crucial role in the aggregation phenomenon,[4] there is evidence that this feature is not an absolute requirement; in one reported example, the nonchiral amphiphile $[Me_2N^+\{(CH_2)_{11}C{\equiv}C{-}C{\equiv}C(CH_2)_{10}\text{-}Me\}_2]Br^-$ forms cylindrical microstructures from aqueous dispersion.[5] It may be noted that the microstructure particle lengths in the compounds described above are generally in the range 10−200 μm and, exceptionally, >1200 μm.[6]

Incorporation of the 1,3-diyne functionality as a prerequirement for self-assembly of such compounds provides particular interest in view of the well-documented topochemical polymerization of diacetylenes.[7] Thus, supramolecular assemblies of some amphiphilic diacetylenic aldonamides can be photochemically polymerized to give polydiacetylenes (PDAs) without significant change in morphology.[3b,c]

Potential uses of modified (e.g., metalated) tubular molecular assemblies such as those described above include materials for electroactive composites[1] and for controlled release;[8] polymerized supramolecular assemblies[9] with biologically active headgroups show promise as biosensors.[10] There is continuing interest in this field, particularly in the synthesis of new classes of diacetylenic amphiphiles and related compounds which may generate unusual morphologies; it is important to identify suitable types of achiral compounds that are easily synthesized and for which analogues can be envisaged. Herein, we describe the synthesis of one such amphiphile **1** and also a symmetrically substituted nonamphiphilic 1,3-diyne **2**, both of which on crystallization from organic solvents form macroscopic helical and cylindrical morphologies, respectively. The crystal

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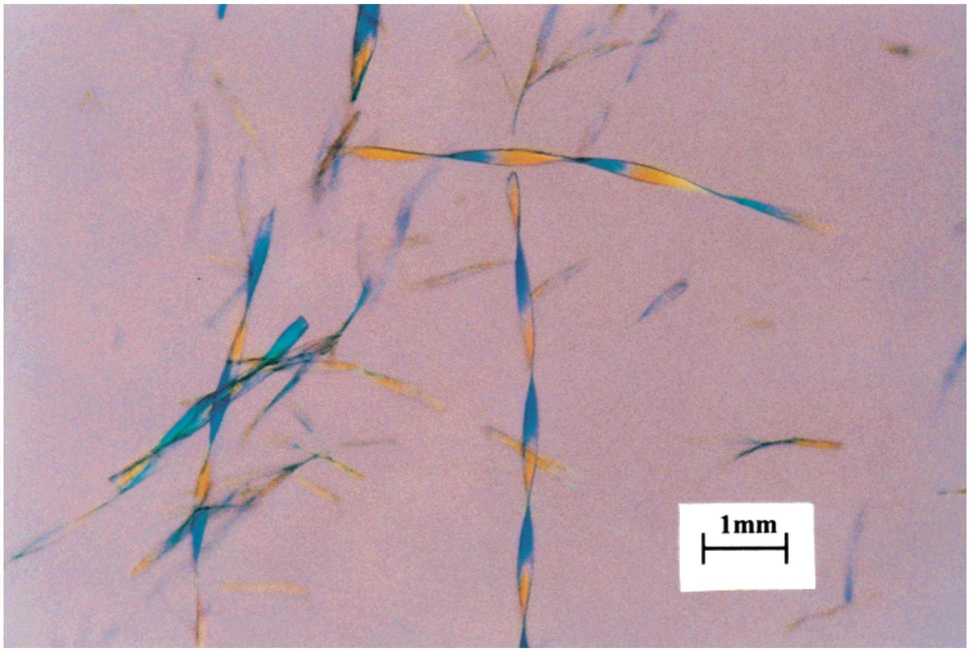
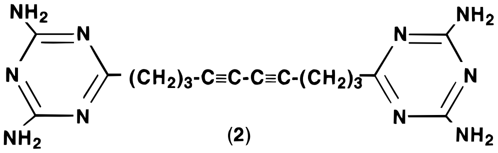


Figure 1. Optical micrograph (530 nm color filter) of the helical form (**1B**) of anhydride **1**.

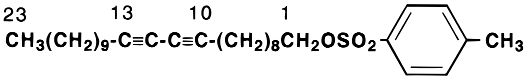
structure of a tosylated diacetylene **3**, structurally related to **1**, is also presented.

$\{CH_3(CH_2)_9\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}(CH_2)_8CO\}_2O$

(**1**)



(**2**)



(**3**)

Results and Discussion

10,12-Tricosadiynoic anhydride (**1**) was prepared[11] by heating commercially available 10,12-tricosadiynoic acid with acetic anhydride; it has been reported previously[12] but spectral characterization data are unavailable. It is a colorless microcrystalline powder (form **1A**) when precipitated from cold diethyl ether but is converted entirely into microcrystalline helical ribbons (form **1B**, Figure 1) when crystallized rapidly (~5 min) in the cold (~5 °C) from petroleum ether (bp 40−60 °C). Examination of ~50 such helices showed, as anticipated, an equal number of species of right- and left-handed chirality; measurements of ~16 helices indicated a mean pitch length of 1.73 ± 0.3 mm, with the longest total length a remarkable 6.4 mm.

It proved impossible to obtain single crystals of **1B** suitable for study by X-ray crystallography. Nevertheless, a powder X-ray diffraction examination of **1B** at 25 °C indicated the existence of a lamellar crystalline phase with a layer spacing of $d = 42.5 \pm 0.5$ Å. Only the odd orders of layer reflection (i.e., 001, 003, 005, 007, 009) were observed. This implies that the electron density profile across the layer has peaks close to $z = 0$ and $z = d$, with a minimum at the center of the layer ($z = d/2$) and suggests that the phase has a noninterdigitated bilayer structure. The fact that the d spacing is much smaller than twice the estimated molecular length of ~30 Å also implies that the molecules are strongly tilted, by ~48° to the normal to the layer. It was demonstrated that melting and resolidifying the sample caused the crystalline lamellar phase to re-form. It was evident from discoloration of the sample (colorless → red-brown) during data collection that a certain degree of polymerization was occurring, but no change in the layer spacing or diffraction pattern was observed, even after 90 h of continuous irradiation at 25 °C. The powder sample (**1A**) gave an almost identical diffraction pattern to **1B** with a layer spacing of $d = 42.1 \pm 0.5$ Å but the diffraction pattern was "spottier", implying that the crystallites were somewhat larger.

As part of a wider study[13] of amphiphiles containing the 1,3-diyne function, we have also prepared the tosylated C_{23}-diacetylene (**3**) with the same hydrophobic alkyl chain as **1**, i.e., $n\text{-}C_{10}H_{21}$, and with a related methylene linkage to the polar headgroup. Compound **3** was obtained as colorless crystals from the reaction of tricosa-10,12-diynyl-1-ol and toluene *p*-sulfonyl chloride.[13] Microcrystalline samples of **3** quickly turn blue on exposure to ambient light due to polydiacetylene formation; also, larger single crystals of **3** shattered on irradiation with a 400 W medium-pressure Hg lamp over 18 h, with formation of polymer. Nevertheless, a single crystal of **3** irradiated in an X-ray beam for 24 h, despite becoming blue in color, was stable and showed no evidence of significant polymerization over this time

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compound 3

S(1)−O(3)	1.4236(15)	S(1)−O(2)	1.4244(15)	S(1)−O(1)	1.5720(14)
S(1)−C(24)	1.7563(18)	O(1)−C(1)	1.468(2)	C(9)−C(10)	1.467(3)
C(10)−C(11)	1.200(3)	C(11)−C(12)	1.379(3)	C(12)−C(13)	1.200(3)
C(13)−C(14)	1.466(3)				
O(3)−S(1)−O(2)	120.09(10)	C(10)−C(11)−C(12)	179.4(2)	O(1)−C(1)−C(2)	108.59(15)
O(2)−S(1)−O(1)	103.68(9)	C(12)−C(13)−C(14)	177.9(2)	C(11)−C(10)−C(9)	178.1(2)
O(2)−S(1)−C(24)	109.98(9)	O(3)−S(1)−O(1)	109.23(8)	C(13)−C(12)−C(11)	179.2(2)
C(1)−O(1)−S(1)	118.76(12)	O(3)−S(1)−C(24)	108.91(9)	C(13)−C(14)−C(15)	112.67(17)
C(10)−C(9)−C(8)	112.72(16)	O(1)−S(1)−C(24)	103.61(8)		

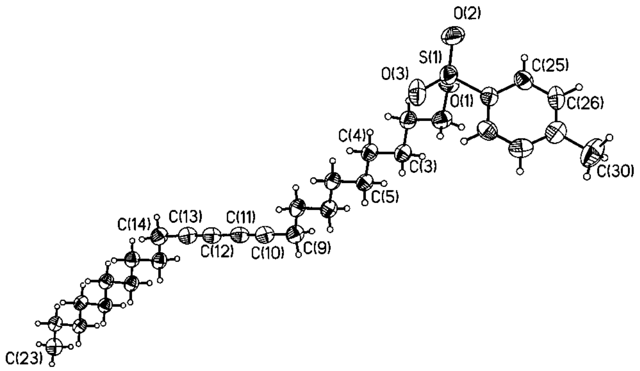

Figure 2. Molecular structure of compound **3** (ORTEP, displacement ellipsoids at 40% probability)

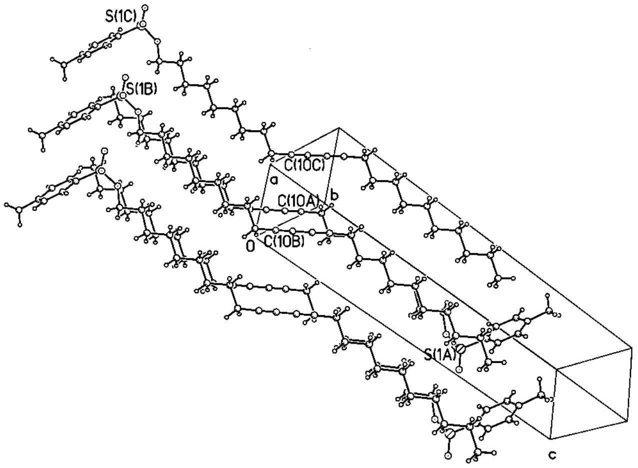

Figure 3. Crystal packing diagram of **3** showing two directions of stacking: molecules A to B; molecules A to C.

scale so that structural analysis by X-ray diffraction was subsequently carried out. Selected geometrical parameters from the X-ray study are given in Table 1 and the molecular structure, with atom labeling, is depicted in Figure 2. Bond lengths and angles of compound **3** are typical of a diacetylene and the extended distance between C(1) and C(23) is 27.326 Å, giving an overall length from methyl group (van der Waals radius 2.0 Å) to headgroup of ~30 Å, as assumed above for the anhydride **1**.

Molecules of **3** stack in two directions, although neither direction corresponds to a crystallographic axis (see Figure 3). The distance between the midpoints of C11 and C12 in molecules A and B is 5.3 Å, where molecule B is related to A by the symmetry operation $-x$, $1 - y$, $-z$. The angle, Φ made by the joining of the two midpoints (the stacking axis) and the acetylene is 43.4°. The molecules are arranged head-to-tail with the distance between C10 in A and B, the potentially reacting atoms being 3.640 Å apart. These values all suggest a potentially reactive monomer.[14,15] Reactive structures tend to have repeat distances of around 5 Å and Φ close to 45°, with the reactive atoms less than 4 Å apart. There is, however, another stacking direction at 107.5° from the first (see Figure 3), in which molecule C is related to A by $1 - x$, $1 - y$, $-z$; the distance between midpoints is 4.685 Å, and Φ is 51.8°, with C10 atoms in A and C being 3.764 Å apart. As with A and B, A and C are aligned head to tail. This choice in direction of polymerization may be why the crystal disintegrates under UV irradiation. No disorder was detectable in the acetylene backbone after 2 days of exposure to X-rays, although the color of the crystal had changed.

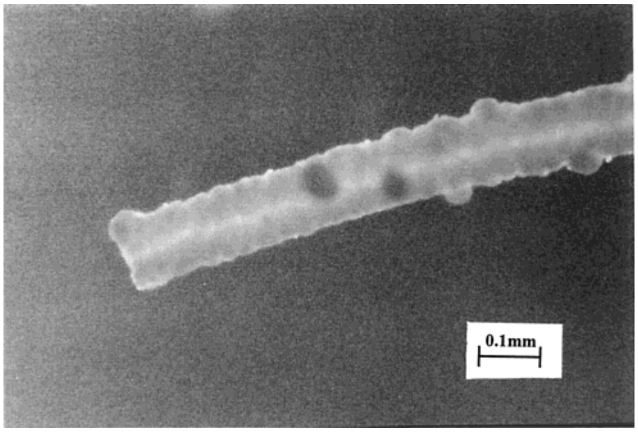

Figure 4. Optical micrograph (polarized light) of **2**.

6,6′-(Deca-4,6-diyne-1,10-diyl)di-2,4-diamino-1,3,5-triazine (**2**) was prepared[16] from the diester $EtO_2C(CH_2)_3C{\equiv}C{-}C{\equiv}C(CH_2)_3CO_2Et$ and biguanide,[17] as a colorless solid that precipitated, in part, in macroscopic cylindrical form (Figure 4) from methanol; from optical microscopy it was noted that individual cylindrical particles were of mean length ~0.5 mm with some examples ~1.0 mm. We have been unable to grow single crystals that would be suitable for an X-ray crystallographic study and powder X-ray diffraction data were relatively uninformative: the sample is crystalline, giving numerous wide-angle Bragg peaks with the largest at a spacing of 5.68 Å; there were no low-angle peaks. An SEM scan of a typical cylindrical particle (Figure 5) clearly shows circular striations consistent with helical formation, although we lack supporting evidence to indicate that a helical morphology precedes

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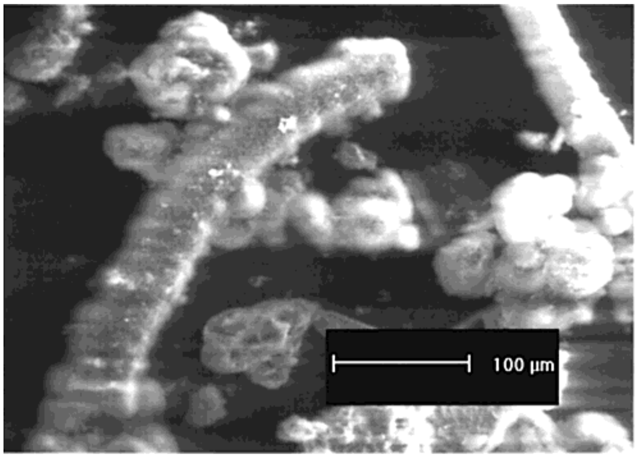
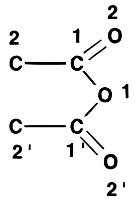


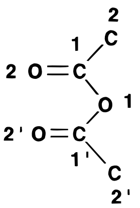
Figure 5. Scanning electron micrograph of **2**.

the cylindrical form (cf. conversion of helical to tubular morphologies in the chemistry of diacetylenic phosphatidylcholines[1]).

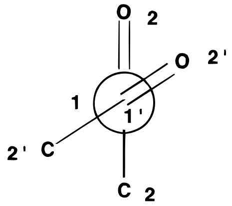
While we lack direct X-ray crystallographic evidence for the packing of achiral molecules **1** and **2** it is interesting to speculate on the origin of the macroscopic chirality. It is known that helical ribbon morphologies can arise from achiral substrates such as graphite[18] and some metals[19] but the phenomenon is rare in organic assemblies (e.g., from the amphiphile described earlier, on crystallization from aqueous gels[5]). It is recognized[20] that introduction of the 1,3-diacetylenic group into lipids will effect a break in cylindrical symmetry of the hydrocarbon chain; pairs of diacetylenic chains can become chiral objects within a lipid bilayer structure, even in the absence of a chiral headgroup. In the presence of the latter, the headgroup chirality can be amplified through the hydrocarbon chains. It is possible for the case of the anhydride (**1**) that the inherent lipid bilayer chirality is accentuated through a headgroup conformational effect. A search through the Cambridge Structural Database[21] reveals more than 200 molecular structures of anhydrides, but the dominant group contains cyclic systems with the anhydride function incorporated into five-, and to a lesser extent, six-membered rings; these anhydrides adopt a cis/cis conformation (**4**) with the interplanar (torsional) angle encompassing O(1)−C(1)−O(2) and O(1)−C(1′)−O(2′) near zero. There is a very small number of reported molecular structures of acyclic anhydrides but, in contrast, they adopt a trans/trans conformation (**5**) with a deviation from coplanarity of the carbonyl groups, with examples showing torsional angles of 6.5°,[22] 28.0°,[23] and 4.3°.[24] For the anhydride **1**, this effect could amplify the chirality through headgroup conformations illustrated in structures **6a** and **6b**.



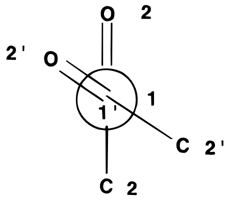
(**4**)



(**5**)



(**6a**)



(**6b**)

Conclusions

Two new classes of achiral 1,3-diynes (**1** and **2**) have been synthesized, both of which self-assemble to afford novel morphologies, including ribbonlike helical material and cylindrical particles; the latter originate from (**2**), which constitutes an unusual example of a self-assembling, symmetrical nonamphiphilic 1,3-diyne, the preparation of which is routine and inexpensive. We are currently engaged in the synthesis of analogous compounds within these categories (cf. **1**, **2**), in studies of their polymerization (cf. ref 25), and in investigation of the morphologies and properties of ensuing polydiacetylenes.

Experimental Section

Melting points were determined using an electrothermal instrument and are uncorrected. IR spectra were recorded on Perkin-Elmer FTIR 1600 or 1430 instruments and calibrated against polystyrene. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker AC 200 or DPX 400 spectrometers; chemical shifts are reported with respect to $SiMe_4$ as reference (positive shifts to high frequency/low field) and J values are given in hertz. EI mass spectra were measured on an upgraded VG MS9 instrument, and the high-resolution mass spectrum was determined at the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea, U.K. Elemental analyses were performed at Heriot-Watt University. Silica gel 60 (200−400 mesh) was used for column chromatography (Merck). Drying agents for solvents were Na/benzophenone [for petroleum ether, diethyl ether, and tetrahydrofuran (THF)] and CaH_2 for dichloromethane. 10,12-Tricosadiynoic acid was obtained commercially (Lancaster Synthesis Ltd); 5,7-dodecadiyn-1,12-dioic acid,[26] biguanide,[17] and tricosa-10,12-diynyl bis(toluene-*p*-sulfonate) (**3**)[13] were prepared as described in the literature.

10,12-Tricosadiynoic Anhydride (1). 10,12-Tricosadiynoic acid (1.80 g; 5.19 mmol) and acetic anhydride (1.87 g; 15.57 mmol) were heated under reflux for 5 h. The excess acetic anhydride was evaporated under reduced pressure and the residual solid was purified by flash chromatography with (40−

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60 °C) petroleum ether/diethyl ether (70:30) as eluant. 10,12-Tricosadiynoic anhydride (1.27 g; 72%) was isolated as a white solid which on recrystallization from petroleum ether (40−60°) afforded a material with a helical morphology, mp 64 °C (differential scanning calorimetry). ν_{max} KBr/cm^{-1}: 2918, 2849 (aliphatic C−H *str*), 1810 (C=O *str*), 1470, 1410 (aliphatic C−H *def*), 1071 (C−O *str*). ^{1}H NMR δ (CDCl$_3$): 0.88 (t, 6H, *J* 6.4, CH_3), 1.13−1.72 (m, 58H), 2.24 (t, 8H, J^1 6.7, CH_2C≡C), 2.29 (t, 4H, J^2 7.3, CH_2CO$_2$). ^{13}C NMR δ (CDCl$_3$): 14.0, 19.1, 22.6, 24.1, 28.2, 28.3, 28.8, 29.0, 29.4, 29.5, 31.8, 35.2, 65.1, 77.6, 169.5. *m*/*z* (FAB, NOBA matrix): 675.5 (1%, [M + 1]$^+$). Found: C, 81.8; H 11.3%. $C_{46}H_{74}O_3$ requires: C, 81.8; H, 11.0%.

Bis-ethyl-5,7-dodecadiyn-1,12-dioate. 5,7-Dodecadiyn-1,-12-dioic acid (2.62 g; 9.41 mmol), absolute ethanol (150 mL), and concentrated sulfuric acid (0.5 mL) were heated under reflux for 4 h. On cooling, saturated aqueous sodium bicarbonate solution was added until no more carbon dioxide evolved. The solvents were evaporated under reduced pressure, and the resulting oil was partitioned between dichloromethane and water (100 mL/100 mL). The organic layer was separated and dried over calcium chloride. Bis-ethyl-10,12-docosadiyn-1,22-dioate (1.22 g; 46%) was isolated as a colorless liquid after flash chromatography, using dichloromethane as eluant. ν_{max} liq. film/cm^{-1}: 2980, 2939 (aliphatic C−H *str*), 1733 (C=O *str*). ^{1}H NMR δ (CDCl$_3$): 1.27 (t, 6H, *J* 7.1, CH_3), 1.86 (quintet, 4H, J^1 7.0, CH$_2$CH_2CH$_2$), 2.35 (t, 4H, J^2 6.9, CH_2C≡C), 2.45 (t, 4H, J^3 7.4, CH_2CO$_2$Et), 4.14 (q, 4H, *J* 7 0.1, CH$_3$CH_2). ^{13}C NMR δ (CDCl$_3$): 14.1, 18.5, 23.4, 32.9, 60.3, 65.9, 76.3, 172.8. *m*/*z* (EI): 278.1492 (M$^{\bullet+}$); 249.1127 (M$^{\bullet+}$ − C$_2$H$_5$); 233.1176 (M$^{\bullet+}$ − C$_2$H$_5$O); $C_{16}H_{22}O_4$ requires: *m*/*z* 278.1518 (M$^{\bullet+}$). $C_{14}H_{17}O_4$ requires: *m*/*z* 249.1159 (M$^{\bullet+}$ − C$_2$H$_5$); $C_{14}H_{17}O_3$ requires: 233.1180 (M$^{\bullet+}$ − C$_2$H$_5$O).

6,6′-(Deca-4,6-diyne-1,10-diyl)di-2,4-diamino-1,3,5-triazine (2). A solution of biguanide[17] (1.44 g; 14.30 mmol) in dry methanol (50 mL) was heated to 40 °C under a nitrogen atmosphere with stirring. Bis-ethyl-5,7-dodecadiyn-1,12-dioate (1.53 g; 5.50 mmol) in dry methanol (20 mL) was slowly added over 10 min with stirring. The reaction was then stirred at 40 °C for 6 h and then for a further 60 h at room temperature. The solvent was evaporated under reduced pressure and the resulting brown solid was purified by flash chromatography using dichloromethane/methanol (98:2) as eluant. 6,6′-(Deca-4,6-diyne-1,10-diyl)di-2,4-diamino-1,3,5-triazine (0.43 g; 22%) was isolated as a white amorphous solid containing cylindrical forms, mp 242 °C (dec). ν_{max} KBr/cm^{-1}: 3335, 3186 (N−H *str*), 2923, 2854 (aliphatic C−H *str*), 1635, 1543 (N−H *def*). ^{1}H NMR δ (DMSO-d_6) 1.78 (quintet, 4H, *J* 7.3, CH$_2$CH_2CH$_2$), 2.39 (t, 4H, J^1 6.9, CH_2C≡C), 2.96 (t, 4H, J^2 7.1, CH_2-triazine), 6.58 (bs, 8H, NH_2). ^{13}C NMR δ (DMSO-d_6) 18.5, 26.1, 37.1, 66.0, 78.3, 167.4, 177.2. *m*/*z* (FAB, NOBA matrix): 353.1950 [21%, (M + H)$^+$]; ($C_{16}H_{20}N_{10}$ + H)$^+$ requires 353.1951. It was demonstrated in separate experiments [MS (FAB, NOBA matrix); LIMA] that the cylindrical portion of the product gave the same mass fragments as the amorphous fraction.

Crystal Structure Determination of Compound (3).[29] Single crystals of **3** were grown by slow diffusion of ether solutions with petroleum ether at room temperature and mounted in epoxy resin glue in a sealed, thin-walled glass capillary for data collection with a Bruker AXS P4 diffractometer[27] at 293 K.

Its characteristics are as follows: colorless plate, 0.12 × 0.72 × 0.34 mm, $C_{30}H_{46}SO_3$ M = 486.73, triclinic, space group, $P\bar{1}$, a = 5.9731(7), b = 8.0690(11), c = , 29.5250(36) Å, α = 95.020(12), β = 93.260(11), γ = 97.480(11)°, U = 1402.1(3) Å^3, Z = 2, μ(Mo Kα) = 0.143 mm^{-1}, data measured = 6446, unique data = 4917, R, wR2 = 0.0619, 0.1172.

Crystallographic computing was performed using the SHELXTL[28] system version 5.1

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(29) Additional crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (see ref 21).