Synthesis, X-ray Structure Analysis and Topochemical Photopolymerization of Substituted 1,6-Bis(2,5-dimethoxyphenyl)hexa-2,4-diynes

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Dedicated to Professor Leslie Leiserowitz, Weizmann Institute of Science, Rehovot, Israel on the occasion of his 65th birthday

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The 1,6-bis(2,5-dimethoxyphenyl)hexa-2,4-diynes **4a–c** were obtained from the corresponding 2,5-dimethoxybenzenes **1** by bromination followed by a copper-catalyzed Grignard reaction with 3-bromoprop-1-yne. Catalyzed coupling of the resulting 3-(2,5-dimethoxyphenyl)prop-1-ynes **3** under Hay conditions gave the hexa-2,4-diynes **4a–c** in good yields. The molecular structures of the diynes **4a** and **4b** were determined by X-ray diffraction analysis. In each crystal structure, an unusual 1,6-synperiplanar conformation of the hexa-2,4-diyne unit is observed, with the 1,6-diphenyl substituents arranged in a coplanar orientation. According to the crystal structure data obtained, irradiation of diynes **4a** and **4b** afforded the deeply-colored, highly-ordered polymers **5a** and **5b** under topochemical control. Oxidation of **4a** and **4b** with cerium(IV) ammonium nitrate gave the corresponding 1,6-bis(2,5-dimethoxyphenyl)hexa-2,4-diyne-1,6-diones **6a** and **6b**.

Introduction

In 1969, Wegner first characterized the solid-state polymerization of conjugated diynes.[1] The polymerization, accomplished by heat, irradiation or pressure, was found to lead to highly ordered polymers.[2,3]

The synthesis of organic metals involves the assembly of a molecular solid of crystalline structure, which favors the metallic state.[4] This implies chain-like structures in which donors and acceptors stack in parallel chains, and a uniform structure where each molecule should be equidistant from its neighbor. Such structures are common in the tetracyanobenzoquinodimethane (TCNQ) salts[5,6] or dicyanobenzoquinodiimine (DCNQI) CT complexes.[7]

By combining the favorable aspects of the highly ordered diyne polymers and the geometric dependency of conductivity of organic metals in the case of quinoid compounds, we sought a convenient method for the synthesis of 2,5-dimethoxyphenyl-substituted diynes as precursors for a wide range of quinone dialkyne derivatives. Our efforts to prepare these diynes are described herein.

Results and Discussion

The 1,6-bis(2,5-dimethoxyphenyl)hexa-2,4-diynes **4a−c** were synthesized starting from the corresponding dimethoxybenzenes **1a−c**[8,9] (Scheme 1). Bromination of **1a−c** in chloroform[10] afforded the bromo derivatives **2a−c** in 79−89% yield. Subsequent Grignard reaction by addition of magnesium turnings and then 3-bromoprop-1-yne in the presence of a catalytic amount of copper(I) chloride[11] gave 3-(2,5-dimethoxyphenyl)prop-1-ynes **3a−c** in 40−58% yield as unstable, colorless liquids. The products were found to oligomerize on standing at room temperature, as detected by electron ionization mass spectrometry. Storage of **3c** at −28 °C for one month also resulted in oligomerized products. The isolated prop-1-ynes **3a−c** were virtually free of allenic isomers; only traces of the corresponding allenes were found by GC-MS analysis. It has been reported that the copper-catalyzed reaction of Grignard reagents with 3-chloroprop-1-yne leads to high yields of the corresponding allenes.[12−15] The use of 3-bromoprop-1-yne instead of 3-chloroprop-1-yne seems to be sufficient to avoid the formation of allenes. In the reaction of phenyl Grignard reagents with 3-bromoprop-1-yne, the presence of methoxy substituents also favours the formation of 3-phenylprop-1-ynes.[16] Coupling of **3a−c**, as catalyzed by CuCl·tmeda in DME under oxygen at 35 °C (Hay conditions), gave **4a−c** in yields of 25−74% as colorless solids, which were found to be light-sensitive in the case of **4a** and **4b**.

In daylight, **4a** turned deep-red to purple after one day, while **4b** turned pink after a few minutes and became violet within one day. Irradiation of **4a** and **4b** with UV light produced similar colors within 1 h. The aforementioned colors are those of the irradiation products prior to work-up. After 6 h of irradiation, work-up of the colored polymers by dichloromethane extraction yielded 9% of **5a** as a red, insoluble solid and 18% of **5b** as a light-violet, insoluble powder. The molecular structure given for **5a** and **5b** in Scheme 2 is typical of a poly(but-1-ene-3-ynylene) obtained from solid-state irradiation of conjugated diynes.[1,17−20] Because of the known insolubility of poly(but-1-ene-3-ynylene), only oligomers of up to $n = 3$ for **5a** and $n = 4$ for **5b** were

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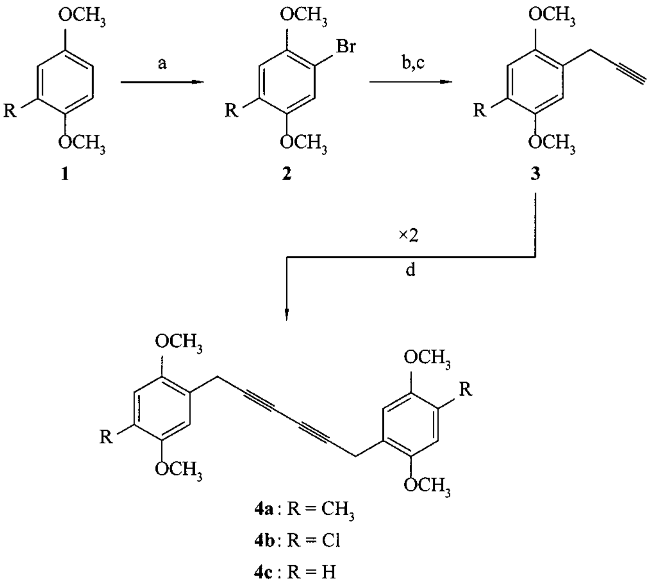


Scheme 1. Synthesis of **4a−c**; reagents and conditions: a) Br_2, $CHCl_3$; 0°C; b) Mg turnings, THF, room temperature, 1 h; c) CuI, 3-bromoprop-1-yne, toluene, room temperature, 1 d; d) CuCl·tmeda, O_2, DME, 35°C, 1 d

Table 1. Selected bond lengths [Å], angles [°], and torsion angles [°] for **4a**

	bond length [Å]		bond length [Å]
C1−C10	1.513(3)	C15−C16	1.511(3)
C10−C11	1.461(3)	C14−C15	1.462(3)
C11−C12	1.195(3)	C13−C14	1.190(3)
C12−C13	1.377(3)		
	bond angle [°]		bond angle [°]
C2−O1−C7	117.2(2)	C17−O3−C22	117.7(2)
C5−O2−C8	116.6(2)	C20−O4−C23	117.0(2)
C11−C10−C1	112.9(2)	C14−C15−C16	115.0(2)
C12−C11−C10	177.3(2)	C13−C14−C15	178.3(2)
C11−C12−C13	178.9(2)	C14−C13−C12	178.9(2)
	torsion angle [°]		torsion angle [°]
C7−O1−C2−C3	1.8(3)	C22−O3−C17−C18	3.4(3)
C8−O2−C5−C6	−1.1(3)	C23−O4−C20−C21	0.7(2)
C6−C1−C10−C11	3.5(3)	C14−C15−C16−C21	0.0(3)

Table 2. Selected bond lengths [Å], angles [°], and torsion angles [°] for **4b**

	bond length [Å]		bond length [Å]
C1−C9	1.514(2)	C12−C20	1.517(2)
C9−C10	1.458(3)	C20−C21	1.461(3)
C10−C11	1.200(3)	C21−C22	1.197(3)
C11−C22	1.369(3)		
	bond angle [°]		bond angle [°]
C2−O1−C7	117.7(2)	C13−O3−C18	117.5(2)
C5−O2−C8	117.4(2)	C16−O4−C19	117.6(2)
C10−C9−C1	114.8(2)	C21−C20−C12	113.4(2)
C11−C10−C9	178.5(2)	C22−C21−C20	178.5(2)
C10−C11−C22	178.4(2)	C21−C22−C11	179.0(2)
	torsion angle [°]		torsion angle [°]
C7−O1−C2−C3	0.7(4)	C18−O3−C13−C14	2.4(4)
C8−O2−C5−C6	5.1(4)	C19−O4−C16−C17	2.0(4)
C6−C1−C9−C10	6.3(4)	C17−C12−C20−C21	0.0(4)

Table 3. Interatomic distances in **4a** and **4b**; the hydrogen atoms of **4a** were refined by inserting them in calculated positions

4a	distance [Å]	**4b**	distance [Å]
C6···C11	2.833(3)	C6···C10	2.851(3)
C11···H6	2.47	C6···H10	2.47(2)
C14···C21	2.894(3)	C17···C21	2.870(3)
C14···H21	2.54	C21···H17	2.50(2)

observed by fast-atom bombardment mass spectrometry (FAB-MS), with correct isotopic peak distributions for $[\mathbf{4a}]_n^+$ (n = 1−2) and $[\mathbf{4b}]_n^+$ (n = 1−3).

The molecular structures of diyne **4a** (Figure 1) and **4b** (Figure 2) were determined by X-ray diffraction analysis. Selected bond lengths and angles are summarized in Tables 1 (**4a**) and 2 (**4b**). The crystal data of **4a** and **4b** are shown in Table 4. Diyne **4a** crystallizes from toluene in space group Cn with $Z = 4$, while diyne **4b** crystallizes from dichloromethane in space group $P2_1/c$ with $Z = 4$. Bond lengths and angles found in **4a** and **4b** fall in the expected ranges,[21] whereas the 1,6-substituents of the hexa-2,4-diyne units are rather unusually arranged in a 1,6-synperiplanar conformation, with torsion angles of 2.3(3)° (C1−C10···C15−C16) in **4a** and of 6.8(3)° (C1−C9···C20−C12) in **4b**. In each crystal structure, the two 1,6-diphenyl substituents are almost coplanar. The 1,4-repulsion between the atoms C6···C11 and C14···C21 in **4a**, and between C6···C10 and C17···C21 in the case of **4b**, as well as the corresponding C···H 1,5-repulsions (see Table 3 for interatomic distances), can be expected to induce a nonplanar conformation. Likewise, force-field calculations (MM+) on **4a** and **4b** showed that a 1,6-anticlinal conformation, with the aromatic rings turned out of the plane, is preferred, indicating that crystal-packing effects are responsible for the observed conformation.

The packing parameters (Table 5) obtained from the crystal structures of diyne **4a** (Figure 3) and **4b** (Figure 4) are in accord with the observed solid-state reactivities. The significance of the intermolecular distances and angles given in Table 5 can be seen in Scheme 2. The correlation between d and distance s usually found in the literature[22] is given by the formula $s = d \sin(\gamma)$. The deviation from γ is $\Delta\gamma$, which is calculated from the formula $\Delta\gamma = |\gamma - 45|$. For significant reactivity, the upper limit for D is 4.3 Å, γ should be near to 45°, and s should be in the range 3.4−4.0 Å. In the crystal, diyne **4a** is stacked along the c axis. The packing parameters, D = 3.978(3) Å and s = 3.622(1) Å, lie in the typical range for topochemical reactivity, whereas $\Delta\gamma$ (11.2°) is remarkably large. Only a few other reactive diynes have $\Delta\gamma > 11°$ [1,6-bis(carbazol-9-yl)hexa-2,4-diyne: $\gamma = 60°$, $\Delta\gamma = 15°$;[23,24] hexa-2,4-diyne-1,6-diyl dibenzoate: $\gamma = 59°$, $\Delta\gamma = 14°$[25]]. The packing parameters of **4a**, which

Table 4. Crystal data and structure refinement for **4a** and **4b**

	4a	**4b**
empirical formula	$C_{24}H_{26}O_4$	$C_{22}H_{20}Cl_2O_4$
molecular mass [g/mol]	378.5	419.3
solvent	toluene	CH_2Cl_2
crystal size [mm]	0.5 × 0.5 × 0.35	0.34 × 0.34 × 0.1
crystal color	colorless	pink
crystal shape	plates	plates
crystal system	monoclinic	monoclinic
space group	*Cn*	$P2_1/c$
cell dimensions		
a [Å]	8.170(1)	18.049(2)
b [Å]	38.25(2)	5.085(1)
c [Å]	6.510(1)	23.149(5)
β [°]	97.60(1)	112.54(1)
V [Å^3]	2016.7(9)	1962.3(6)
$d_{calcd.}$ [g/cm^3]	1.25	1.42
Z	4	4
F(000)	808	872
T [K]	193	193
hkl range (min./max.)	0/10, 0/50, −8/8	0/23, −6/0, −30/28
$(\sin\Theta/\lambda)_{max}$ [Å^{-1}]	0.66	0.66
μ [mm^{-1}]	0.08	0.36
no. of reflns. colld.	2594	4876
no. of indep. reflns.	2594	4733
no. of reflns. observed	2439	3325
R_{int}	–	0.044
refined parameters	259	333
$(\Delta/\sigma)_{max}$	< 0.01	< 0.01
R [$I > 2\sigma(I)$]	0.039	0.041
R_w	0.098	0.102
S (gof) on F^2	1.12	1.12
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$ [e Å^{-3}]	0.19/−0.24	0.40/−0.43

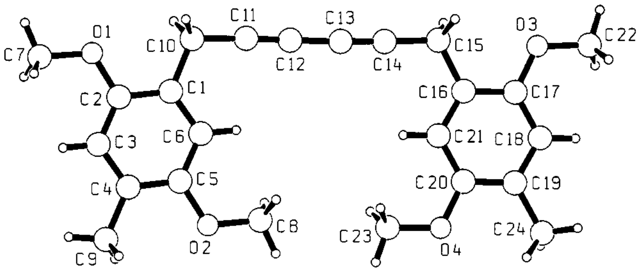


Figure 1. Molecular structure of **4a** in the solid state; H atoms are not numbered for clarity

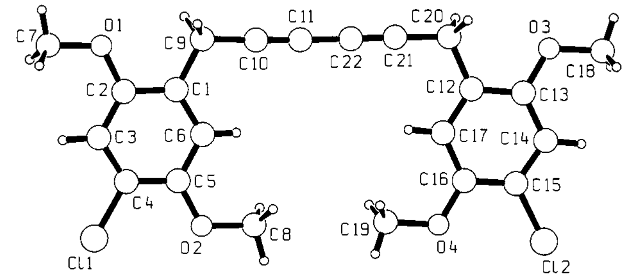


Figure 2. Molecular structure of **4b** in the solid state; H atoms are not numbered for clarity

fall at the upper end of the range of values for significant reactivity, may account for the fact that polymerization of **4a** is rather slow and that light sensitivity is relatively low.

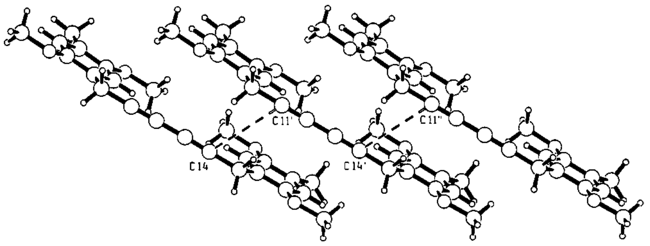


Figure 3. Stacking arrangement of **4a** in crystal along axis *c* with the short distances of $D = 3.978(3)$ Å between alkyne C atoms C11 and C14 of neighboring molecules

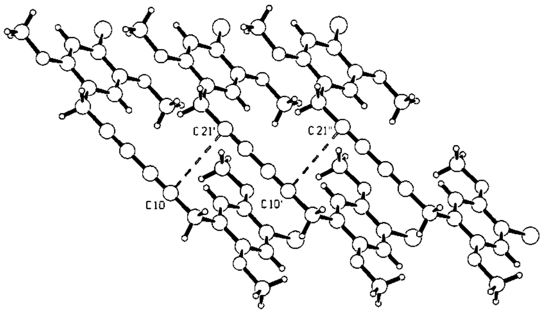
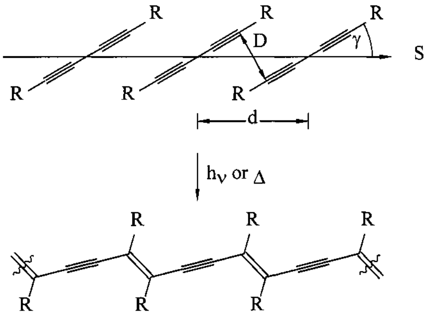


Figure 4. Stacking arrangement of **4b** in crystal along axis *b* with the short distances of $D = 3.585(3)$ Å between alkyne C atoms C10 and C21 of neighboring molecules



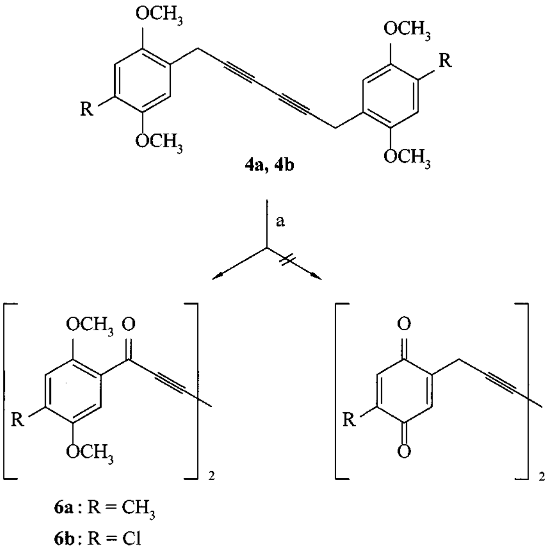
Scheme 2. 1,4-Polyaddition of the conjugated diynes **4a** and **4b** to poly(but-1-ene-3-ynylene)s **5a** and **5b** {**4a**, **5a**: R = $CH_2C_6H_2$(4-Me)[2,5-(MeO)$_2$]; **4b**, **5b**: R = $CH_2C_6H_2$(4-Cl)[2,5-(MeO)$_2$]}; the angle between the axis *S* and the diyne rods is γ; the distance of neighboring diyne units in the direction of *S* is *d*; the distance between the carbon atoms that become bonded during polymerization is *D*

Table 5. Stacking parameters of **4a** and **4b**; for definition of *D*, *d*, and γ see Scheme 2; for Δγ and *s* see text

	D [Å]	*d* [Å]	γ [°]	Δγ [°]	*s* [Å]
4a	3.978(3)	6.510(1)	33.81(1)	11.19(1)	3.622(1)
4b	3.585(3)	5.085(1)	44.07(1)	0.93(1)	3.537(1)

Diyne **4b** shows a stacked structure along the crystallographic *b* axis, with $D = 3.585(3)$ Å. Despite the nearly optimal packing parameters of $\gamma = 44.1°$ and $s = 3.537(1)$ Å, the color of the resulting polymer is violet instead of the ideally dark blue.[26,27] This indicates a slight twisting of the polymer backbone owing to the repulsive interactions between the 2,5-dimethoxyphenyl substituents of the polymer.

Oxidation of **4a** and **4b** with cerium(IV) ammonium nitrate [$Ce(NH_4)_2(NO_3)_6$, CAN] in aqueous acetonitrile[28] gave the corresponding ketones **6a** and **6b** (Scheme 3), although the latter could not be isolated and was only characterized by mass spectrometry. Similar treatment of **4c** afforded only an unidentifiable red oil. Attempted oxidations of **4a−c** under various other conditions (with CrO_3, $KMnO_4$ or HNO_3, or by anodic oxidation) also failed to give the corresponding quinones. Attempted demethylation of **4a−c** using an excess of HBr in acetic acid or with BBr_3 in dichloromethane was unsuccessful and the unreacted diynes **4a−c** were recovered almost quantitatively.



Scheme 3. Oxidation of diynes **4a** and **4b** to the corresponding ketones **6a** and **6b**; reagents and conditions: a) CAN, aqueous acetonitrile, room temperature, 30 min

Experimental Section

General: Melting points: Büchi Melting Point B-540 (Switzerland), open capillary tube. − IR: Bruker IFS 66. − UV/Vis: HP 8452 A (diode array). − NMR: Bruker AC 300 (300 and 75.5 MHz, for ^{1}H and ^{13}C, respectively), chemical shifts are relative to the solvent signal indicated (internal standard TMS). − MS: Finnigan 3200 (low-resolution electron ionization; 70 eV), Vacuum Generators Micromass ZAB-2F (high-resolution electron ionization; 70 eV), and Jeol JMS-700 (fast-atom bombardment). − Elemental analyses: Heraeus CHN-O-Rapid.

Diethyl ether, dimethoxyethane (DME), tetrahydrofuran (THF), and benzene were distilled from sodium benzophenone ketyl prior to use. Dichloromethane, cyclohexane, *n*-hexane, petroleum ether (boiling range 30−75°C), and tetramethylethylenediamine (TMEDA) were distilled from calcium hydride. All reagents were purified according to standard methods before use unless otherwise indicated. All reactions were carried out under argon. − The following compounds have been reported previously in the literature and were prepared as described or according to published procedures: 1,4-dimethoxybenzene,[8] 1,4-dimethoxy-2-methylbenzene,[9] 1-bromo-2,5-dimethoxybenzene,[10] 1-bromo-2,5-dimethoxy-4-methylbenzene,[10] and 1-bromo-4-chloro-2,5-dimethoxybenzene.[10] 3-Bromoprop-1-yne (80% solution in toluene) and 1-chloro-2,5-dimethoxybenzene were purchased from Aldrich and used without further purification.

3-(2,5-Dimethoxy-4-methylphenyl)prop-1-yne (3a): To a suspension of 2.67 g (110 mmol) magnesium turnings in 10 mL of THF, a solution of 23.11 g (100 mmol) **2a** in 100 mL of THF was added at such a rate so as to maintain a gentle reflux. After the addition, the mixture was refluxed for 45 min. Excess magnesium turnings were removed by filtration and at 0°C the Grignard solution was added quickly to a stirred suspension of 144 mg (1 mmol) of copper(I) chloride and 11.90 g (100 mmol) of 3-bromoprop-1-yne in 50 mL of THF. After stirring for 12 h at room temperature, 200 mL of cyclohexane was added, the mixture was concentrated in vacuo to a volume of 180 mL, and then poured into a solution of 20 g of ammonium chloride and 0.4 g of sodium cyanide in 200 mL of water. After stirring for 10 min, the organic layer was separated and the aqueous layer was extracted with cyclohexane (4 × 100 mL). The combined organic extracts were washed with water (1 × 100 mL), dried with $MgSO_4$, and concentrated in vacuo. Distillation of the residue gave 7.56 g (39.7 mmol; 40%) of **3a** as a colorless, unstable liquid, b.p. 87°C (0.2 Torr), $n_D^{20} = 1.5420$. − IR (NaCl): $\tilde{\nu} = 3291$ cm^{-1} (vs, $\equiv$C−H), 2996 (vs), 2938 (s), 2831 (s), 2119 (m, −C$\equiv$CH), 1941 (w), 1697 (w), 1509 (vs), 1465 (vs), 1419 (vs), 1399 (vs), 1376 (m), 1327 (m), 1281 (m), 1215 (vs), 1180 (m), 1105 (m), 1046 (vs), 1004 (m), 857 (vs), 749 (m), 663 (vs). − ^{1}H NMR (C_6D_6): $\delta = 7.10$ (s, 1 H, 6-H), 6.47 (s, 1 H, 3-H), 3.64 (d, $^4J_{HH} = 2.7$ Hz, 2 H, C*H*$_2$CCH), 3.48 (s, 3 H, CH_3O), 3.33 (s, 3 H, CH_3O), 2.27 (s, 3 H, CCH_3), 1.99 (t, $^4J_{HH} = 2.7$ Hz, 1 H, CH_2CC*H*). − ^{13}C NMR (C_6D_6): $\delta = 152.19$ (*C*OCH$_3$), 150.79 (*C*OCH$_3$), 125.58 (*C*CH$_2$CCH), 122.58 (*C*CH$_3$), 113.73 (6-CH), 111.94 (3-CH), 82.51 (CCH$_2$*C*CH), 70.56 (CCH$_2$C*C*H), 55.50 (CO*C*H$_3$), 55.44 (CO*C*H$_3$), 19.44 (C*C*H$_2$CCH), 16.33 (C*C*H$_3$). − MS (70 eV); *m/z* (%): 190 (100) [M$^+$], 175 (83) [M$^+$ − CH$_3$], 160 (30) [M$^+$ − 2 × CH$_3$], 132 (28) [M$^+$ − 2 × CH$_3$ − CO]. − $C_{12}H_{14}O_2$ (190.25): calcd. 190.0994; found 190.1028 (MS).

1,6-Bis(2,5-dimethoxy-4-methylphenyl)hexa-2,4-diyne (4a): A solution of 7.56 g (39.7 mmol) **3a** in 15 mL of DME was added dropwise at 35−36°C to a suspension of 3.92 g (39.6 mmol) of copper(I) chloride and 6.90 g (59.4 mmol) of TMEDA in 75 mL of DME. At 35−36°C, a stream of oxygen was bubbled through this mixture for 50 min. The reaction mixture was then poured into 300 mL of water. The resulting precipitate was filtered off and recrystallized twice from benzene yielding 5.54 g (14.7 mmol; 74%) of **4a** as colorless, light-sensitive plates, m.p. 127°C. − IR (KBr): $\tilde{\nu} = 3046$ cm^{-1} (w), 3002 (m), 2952 (m), 2829 (m), 1510 (vs), 1465 (m), 1416 (m), 1398 (m), 1212 (vs), 1046 (vs), 858 (m), 823 (m), 654 (w). − UV/Vis (CH_2Cl_2): λ (ε) = 224 nm (13081), 294 (7832). − ^{1}H NMR (C_6D_6): $\delta = 6.98$ (s, 2 H, 6-H), 6.44 (s, 2 H, 3-H), 3.67 (s, 4 H, C*H*$_2$CC), 3.36 (s, 6 H, CH_3O), 3.27 (s, 6 H, CH_3O), 2.27 (s, 3 H, CCH_3). − ^{13}C NMR (C_6D_6): $\delta = 152.24$ (*C*OCH$_3$), 150.77 (*C*OCH$_3$), 125.79 (*C*CH$_2$CC), 122.14 (*C*CH$_3$), 113.92 (6-CH), 111.98 (3-CH), 76.24 (CCH$_2$*C*C), 67.95 (CCH$_2$C*C*), 55.55 (CO*C*H$_3$), 55.36 (CO*C*H$_3$), 20.32 (C*C*H$_2$CC), 16.40 (C*C*H$_3$). − MS (70 eV); *m/z* (%): 378 (100) [M$^+$], 363 (7) [M$^+$ − CH$_3$], 333 (12) [M$^+$ − 3 × CH$_3$], 189 (16) [M$^+$ − $C_6H_3(OCH_3)_2(CH_3)CH_2C_2$]. − $C_{24}H_{26}O_4$ (378.47): calcd. 378.1831; found 378.1822 (MS); calcd. C 76.17, H 6.92; found C 75.95, H 6.93.

3-(4-Chloro-2,5-dimethoxyphenyl)prop-1-yne (3b): To a suspension of 4.01 g (165 mmol) of magnesium turnings in 10 mL of THF, a suspension of 37.72 g (150 mmol) of **2b** in 150 mL of THF was added at such a rate so as to maintain a gentle reflux. After stirring for 1 h, the mixture was refluxed for a further 1 h. The resulting Grignard solution was filtered and added dropwise to an ice-cooled suspension of 215 mg (1.5 mmol) of copper(I) bromide and 17.25 g (145 mmol) of 3-bromoprop-1-yne in 30 mL of THF. The reaction mixture was stirred for 16 h, diluted with 100 mL of cyclohexane, and then concentrated to a volume of 100 mL. The residue was poured into a solution of 10 g of ammonium chloride and 1 g of sodium cyanide in 100 mL of water. The organic layer was separated and the aqueous phase was extracted with diethyl ether (3 × 100 mL). Distillation of the combined organic layers gave 15.84 g (75.3 mmol; 54%) of **3b** as a colorless, unstable liquid, which solidified on standing, b.p. 84°C (0.1 Torr), m.p. 34−35°C. − IR (KBr): $\tilde{\nu}$ = 3295 cm^{-1} (s, ≡C−H), 2939 (m), 2842 (m), 2120 (w, −C≡CH), 1501 (vs), 1465 (m), 1415 (m), 1389 (m), 1213 (vs), 1180 (m), 1131 (m), 1038 (s), 851 (m), 823 (m), 725 (w). − ^{1}H NMR (C_6D_6): δ = 7.08 (s, 1 H, 6-H), 6.67 (s, 1 H, 3-H), 3.45 (d, $^4J_{HH}$ = 2.8 Hz, 2 H, C*H*$_2$CCH), 3.41 (s, 3 H, CH_3O), 3.27 (s, 3 H, CH_3O), 1.98 (t, $^4J_{HH}$ = 2.8 Hz, 1 H, CH_2CC*H*). − ^{13}C NMR (C_6D_6): δ = 151.04 (*C*OCH$_3$), 149.71 (*C*OCH$_3$), 124.17 (*C*CH$_2$CCH), 121.41 (CCl), 114.14 (6-CH), 112.95 (3-CH), 81.54 (CCH$_2$*C*CH), 71.23 (CCH$_2$C*C*H), 56.29 (CO*C*H$_3$), 55.41 (CO*C*H$_3$), 19.38 (C*C*H$_2$CCH). − MS (70 eV); *m*/*z* (%): 210 (100) [M$^+$], 195 (61) [M$^+$ − CH$_3$], 180 (10) [M$^+$ − 2 × CH$_3$], 152 (20) [M$^+$ − 2 × CH$_3$ − CO]. − $C_{11}H_{11}ClO_2$ (210.66): calcd. 210.0448; found 210.0449 (MS).

1,6-Bis(4-chloro-2,5-dimethoxyphenyl)hexa-2,4-diyne (4b): To a stirred solution of 5.26 g (25 mmol) of **3c** in 10 mL DME at 30−35°C was slowly added a solution of 0.741 g (7.5 mmol) of copper(I) chloride and 1.307 g (11.25 mmol) of TMEDA in 40 mL of DME. Oxygen was then bubbled through this solution under vigorous stirring for 75 min at 35−36°C. The reaction mixture was subsequently poured into 200 mL of water and extracted with dichloromethane (4 × 100 mL). The combined organic layers were concentrated under reduced pressure. After storage for 1 d at 4°C, the resulting precipitate was filtered off and recrystallized twice from benzene to yield 1.33 g (3.18 mmol; 25%) of **4b** as colorless, light-sensitive plates, m.p. 174−175°C. − IR (KBr): $\tilde{\nu}$ = 3007 cm^{-1} (m), 2957 (m), 2838 (m), 1503 (vs), 1460 (m), 1408 (m), 1386 (m), 1211 (vs), 1178 (s), 1130 (s), 1056 (vs), 1037 (s), 849 (m), 823 (m), 725 (w). − UV/Vis (CH_2Cl_2): λ (ε) = 234 nm (12447), 296 (9914). − ^{1}H NMR (C_6D_6): δ = 6.91 (s, 2 H, 6-H), 6.66 (s, 2 H, 3-H), 3.48 (s, 4 H, CH_2CC), 3.27 (s, 6 H, CH_3O), 3.01 (s, 6 H, CH_3O). − ^{13}C NMR (C_6D_6): δ = 150.99 (*C*OCH$_3$), 149.80 (*C*OCH$_3$), 123.53 (*C*CH$_2$CC), 121.76 (CCl), 114.19 (6-CH), 113.20 (3-CH), 75.63 (CCH$_2$*C*C), 68.09 (CCH$_2$C*C*), 56.18 (CO*C*H$_3$), 55.35 (CO*C*H$_3$), 20.18 (C*C*H$_2$CC). − MS (70 eV); *m*/*z* (%): 418 (100) [M$^+$], 403 (10) [M$^+$ − CH$_3$], 373 (10) [M$^+$ − 3 × CH$_3$], 353 (11) [M$^+$ − 2 × CH$_3$ − ^{35}Cl]. − $C_{22}H_{20}Cl_2O_4$ (419.31): calcd. 418.0739; found 418.0759 (MS); calcd. C 63.02, H 4.81, Cl 16.91; found C 62.93, H 4.82, Cl 16.99.

3-(2,5-Dimethoxyphenyl)prop-1-yne (3c): To a suspension of 3.55 g (146 mmol) of magnesium turnings in 10 mL of THF, 8.75 g (40 mmol) of **2c** and 0.5 mL of bromoethane were added. After initiation of the Grignard reaction, a solution of 20 g (92 mmol) of **2c** in 20 mL of THF was added over a period of 45 min. After stirring for 1 h, the mixture was gently refluxed for a further 1 h. The excess magnesium turnings were filtered off and the clear Grignard solution was slowly added at 0°C to a suspension of 190 mg (1.32 mmol) of copper(I) bromide and 19.33 g (130 mmol) of 3-bromoprop-1-yne in 75 mL of THF. After stirring for 24 h, 100 mL of cyclohexane was added and the solution was concentrated in vacuo to a volume of 120 mL. The concentrated mixture was poured into a solution of 10 g of ammonium chloride and 1 g of sodium cyanide in 100 mL of water and extracted with diethyl ether (4 × 100 mL). The combined ethereal extracts were dried with $MgSO_4$ and concentrated in vacuo. Purification of the residue by distillation gave 11.46 g (65.1 mmol; 49%) of **3c** as a colorless, unstable liquid, b.p. 126−128°C (8 Torr), n_D^{20} = 1.5394. − IR (KBr): $\tilde{\nu}$ = 3292 cm^{-1} (s, ≡C−H), 2999 (m), 2950 (m), 2908 (m), 2834 (m), 2120 (w, −C≡CH), 1609 (w), 1499 (vs), 1465 (m), 1431 (m), 1279 (m), 1219 (vs), 1179 (s), 1156 (m), 1114 (m), 1048 (s), 1027 (s), 801 (m), 712 (m), 697 (m). − ^{1}H NMR (C_6D_6): δ = 7.35 (d, $^4J_{HH}$ = 2.9 Hz, 1 H, 6-H), 6.67 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 3.0 Hz, 1 H, 4-H), 6.42 (d, $^3J_{HH}$ = 8.8 Hz, 1 H, 3-H), 3.59 (d, $^4J_{HH}$ = 2.6 Hz, 2 H, C*H*$_2$CCH), 3.41 (s, 3 H, CH_3O), 3.27 (s, 3 H, CH_3O), 1.97 (t, $^4J_{HH}$ = 2.6 Hz, 1 H, CH_2CC*H*). − ^{13}C NMR ($CDCl_3$): δ = 154.39 (*C*OCH$_3$), 151.34 (*C*OCH$_3$), 126.05 (*C*CH$_2$CCH), 115.70 (6-CH), 112.51 (3-CH), 111.14 (4-CH), 81.90 (sCCH$_2$*C*CH), 70.98 (CCH$_2$C*C*H), 55.35 (CO*C*H$_3$), 55.26 (CO*C*H$_3$), 19.68 (C*C*H$_2$CCH). − MS (70 eV); *m*/*z* (%): 176 (100) [M$^+$], 161 (61) [M$^+$ − CH$_3$], 118 (33) [M$^+$ − 2 × CH$_3$ − CO]. − $C_{11}H_{12}O_2$ (176.22): calcd. 176.0837; found 176.0844 (MS).

1,6-Bis(2,5-dimethoxyphenyl)hexa-2,4-diyne (4c): To a solution of 3.52 g (20 mmol) of **3c** in 10 mL of DME, a suspension of 0.594 g (6 mmol) of copper(I) chloride and 1.046 g (9 mmol) of TMEDA in 40 mL of DME was slowly added at 30−35°C. At 35−36°C, a stream of oxygen was passed through the mixture for 55 min. The reaction mixture was subsequently quenched with 200 mL of water, extracted with cyclohexane (4 × 100 mL), and the combined extracts were concentrated. After storage for 1 d at 4°C, the crystals deposited were filtered off and recrystallized twice from *n*-hexane yielding 1.46 g (4.17 mmol; 42%) of **4c** as light-yellow needles, m.p. 88°C. − IR (KBr): $\tilde{\nu}$ = 3005 cm^{-1} (m), 2964 (m), 2836 (m), 1618 (w), 1499 (vs), 1465 (m), 1442 (m), 1425 (m), 1277 (s), 1241 (s), 1216 (s), 1112 (s), 1052 (s), 1024 (s), 860 (m), 795 (s), 714 (s). − UV/Vis (CH_2Cl_2): λ (ε) = 226 nm (14784), 294 (8705). − ^{1}H NMR (C_6D_6): δ = 7.20 (d, $^4J_{HH}$ = 3.0 Hz, 2 H, 6-H), 6.68 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 3.0 Hz, 2 H, 4-H), 6.39 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, 3-H), 3.58 (s, 4 H, CH_2CC), 3.34 (s, 6 H, CH_3O), 3.23 (s, 6 H, CH_3O). − ^{13}C NMR (C_6D_6): δ = 154.38 (*C*OCH$_3$), 151.29 (*C*OCH$_3$), 125.54 (*C*CH$_2$CC), 115.46 (6-CH), 113.13 (3-CH), 111.43 (4-CH), 75.76 (CCH$_2$*C*C), 68.17 (CCH$_2$C*C*), 55.40 (CO*C*H$_3$), 55.22 (CO*C*H$_3$), 20.51 (C*C*H$_2$CC). − MS (70 eV); *m*/*z* (%): 350 (58) [M$^+$], 335 (15) [M$^+$ − CH$_3$], 319 (22) [M$^+$ − CH$_3$O], 199 (27) [M$^+$ − $(CH_3O)_2C_6H_3CH_2$], 182 (89) [$C_{13}H_{10}O^+$], 151 (100) [$C_9H_{11}O_2^+$]. − $C_{22}H_{22}O_4$ (350.42): calcd. 350.1518; found 350.1525 (MS); calcd. C 75.41, H 6.33; found C 75.26, H 6.44.

Poly[1,2-bis(2,5-dimethoxy-4-methylbenzyl)but-1-en-3-ynylene] (5a): 15.6 mg (41.2 μmol) of powdered **4a** was irradiated with UV light for 6 h. To remove unreacted monomer, the deep-red solid was extracted with dichloromethane for 2 h and then dried in vacuo to yield 1.4 mg (9%) of **5a** as a red solid, m.p. > 320°C. − MS (FAB); *m*/*z* (%): 1134 (1) [$(C_{24}H_{26}O_4)_3^+$], 756 (9) [$(C_{24}H_{26}O_4)_2^+$], 378 (100) [$C_{24}H_{26}O_4^+$].

Poly[1,2-bis(4-chloro-2,5-dimethoxybenzyl)but-1-en-3-ynylene] (5b): A sample of 10.2 mg (24.4 μmol) of powdered **4b** was irradiated with UV light for 6 h. The resulting violet solid was then extracted with dichloromethane for 4 h to remove unreacted monomer. Drying in vacuo to constant mass gave 1.8 mg (18%) of **5b** as a light-violet solid, m.p. > 320°C. − MS (FAB); *m*/*z* (%): 1680 (8) [$(C_{22}H_{20}{}^{35}Cl_2O_4)_4^+$ + 6], 1258 (17) [$(C_{22}H_{20}{}^{35}Cl_2O_4)_3^+$ + 4], 838 (38) [$(C_{22}H_{20}{}^{35}Cl_2O_4)_2^+$ + 2], 418 (100) [$C_{22}H_{20}{}^{35}Cl_2O_4^+$].

1,6-Bis(2,5-dimethoxy-4-methylphenyl)hexa-2,4-diyne-1,6-dione (6a): To a solution of 113 mg (0.3 mmol) of **4a** in 15 mL of acetonitrile, a solution of 877 mg (1.6 mmol) of CAN in 10 mL of water was added dropwise. The mixture was stirred for 30 min at room temperature. The resulting precipitate was filtered off and recrystallized from benzene to give 43 mg (0.11 mmol; 35%) of **6a** as yellow needles, m.p. 190−191°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3073 cm^{-1} (m), 2950 (w), 2830 (w, OCH_3), 2129 (m, $C\equiv C$), 1591 (vs, $C=O$), 1505 (s), 1470 (m), 1403 (m), 1223 (vs), 1176 (s), 1042 (vs, OCH_3), 963 (m), 878 (m), 793 (m), 757 (m), 685 (w). − ^1H NMR ($CDCl_3$): δ = 7.35 (s, 2 H, 6-H), 6.81 (s, 2 H, 3-H), 3.90 (s, 6 H, CH_3O), 3.82 (s, 6 H, CH_3O), 2.27 (s, 3 H, CCH_3). − ^{13}C NMR ($CDCl_3$): δ = 173.58 ($C=O$), 155.21 ($\mathit{C}OCH_3$), 151.89 ($\mathit{C}OCH_3$), 137.30 ($\mathit{C}CH_2CC$), 123.62 ($\mathit{C}CH_3$), 115.68 (6-CH), 111.03 (3-CH), 83.64 ($CCH_2\mathit{C}C$), 74.44 ($CCH_2C\mathit{C}$), 56.65 ($CO\mathit{C}H_3$), 55.90 ($CO\mathit{C}H_3$), 17.16 ($C\mathit{C}H_3$). − MS (70 eV); *m/z* (%): 406 (100) [M^+], 391 (9) [$M^+ - CH_3$], 363 (6) [$M^+ - CH_3 - CO$], 179 (41) [$CH_3C_6H_2(OCH_3)_2CO^+$]. − $C_{24}H_{22}O_6$ (406.44): calcd. 406.1416; found 406.1449 (MS).

Crystal Structure Determinations: Crystal data of **4a** and **4b** are presented in Table 4. Selected bond lengths and angles are given in Tables 1 and 2. Data collection was performed with an Enraf-Nonius CAD4 diffractometer (Mo-K_α radiation, graphite monochromator, $\omega-2\theta$ scan with $\theta = 2-28°$). Intensities were corrected for absorption effects (numerical) in the case of **4b**. The structures were solved by direct methods (**4a**: SHELXS-97[29]; **4b**: SHELXS-86[30]) and refined by full-matrix least-squares methods based on F^2 with all measured reflections (**4a**: SHELXL-97[29]; **4b**: SHELXL-93[31]). All non-hydrogen atoms were refined using anisotropic temperature factors. For **4a** the hydrogen atoms were inserted in calculated positions. All hydrogen atoms of **4b** were refined using isotropic temperature factors. Further details on the structure determinations are given in Table 4.[32]

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[32] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk], on quoting the depository numbers CCDC-102931 and -102930.

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