Mesomorphic Donor-Acceptor-substituted 1,4-Distyrylbenzenes

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The (*E,E*)-distyrylbenzenes **1a**, **b** with terminal donor-acceptor substitution were prepared by a sequence of four reaction steps including two Wittig-Horner reactions. The products form smectic mesophases, are photostable, and should permit an electric orientation/reorientation, because of their strong dipole character.

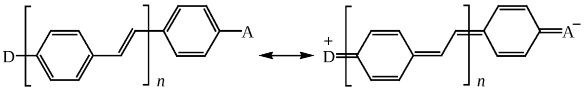
Key words: Liquid Crystals, Push-Pull Effect, Wittig-Horner Reaction

Introduction

Conjugated oligomers with terminal donor-acceptor substitution attract increasing attention in organic chemistry because of their outstanding and not seldom unexpected properties in materials science [1 – 4]. Although a variety of oligo(1,4-phenylene-vinylene)s with terminal donor-acceptor substitution (DAOPVs **1**, Scheme 1) are known [5 – 22], the number of thermotropic liquid crystals among them is very low and is confined to monomers (*n* = 1), that means to certain push-pull substituted (*E*)-stilbenes [23 – 31]. The behavior of conjugated molecules, which are highly polar and form mesophases by self-organization, is very interesting for various applications of liquid crystals [3].

A big disadvantage of stilbenes (*n* = 1), compared to higher OPVs ($n \geq 2$), is due to their light sensitivity. Stilbenes show four types of photoreactions in the first excited singlet state S_1: $E \rightleftarrows Z$ isomerization, concerted [$2\pi_s + 2\pi_s$] cycloadditions, [$6\pi_s$] electrocyclic ring closures, and photo-crosslinking by statistical CC bond formation [32]. The extended conjugation in OPVs ($n \geq 2$) prevents in their S_1 state the first three processes and permits only the crosslinking by irradiation with energy-rich UV light (λ = 254 nm) [32]. The intersystem crossing (ISC) rate is normally very low in OPVs ($n \geq 1$), so that triplet photoreactions can also be neglected.

Among the multiple DAOPVs ($n \geq 2$) which were studied in the past, thermotropic LC phases could not be found. Therefore, our chances to realize this concept were low in the beginning. (*E,E*)-1,4-Distyrylbenzenes with short alkoxy chains or small or large dialkylamino groups and cyano or nitro groups do not form mesophases [3, 4]. We decided to study (*E,E*)-1,4-distyrylbenzenes as calamitic mesogens with cyano groups as acceptors A and long flexible alkoxy groups as donors D. After all experience with liquid crystals, these preconditions seemed to be the most promising. The π-π interaction of (*E,E*)-1,4-distyrylbenzenes has to be sustained by highly effective van der Waals interactions of saturated chains.



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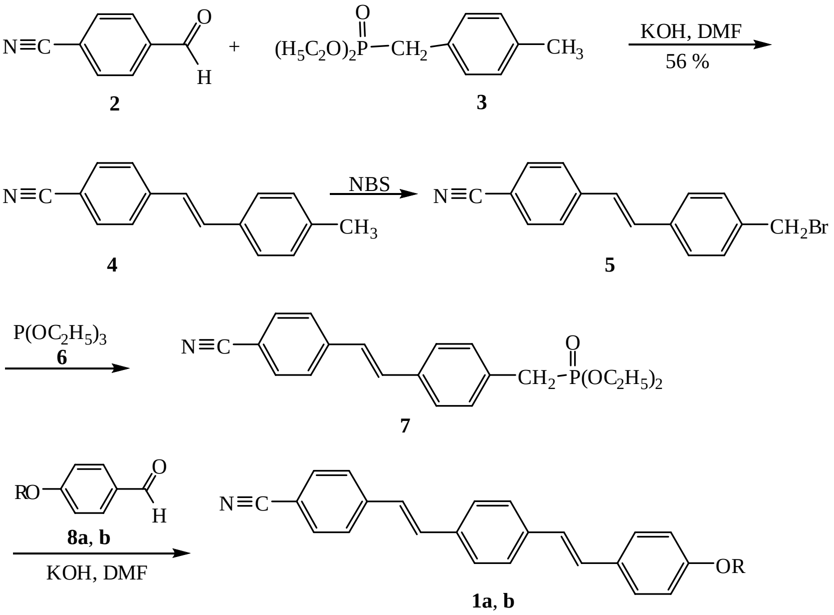
Scheme 1. DAOPVs; donor-acceptor-substituted oligo(1,4-phenylene-vinylene)s.

Results and Discussion

The synthetic approach to the target compounds **1a**, **b** started with the preparation of 4-((*E*)-2-*p*-tolylvinyl)benzonitrile (**4**) by Wittig-Horner reaction of aldehyde **2** and phosphonate **3** [33]. NBS bromination afforded **5** which was transformed in an Arbusov reaction with triethylphosphite **6** to the phosphonate **7**. Wittig-Horner reaction of **7** and 4-hexyloxybenzaldehyde (**8a**) [34, 35] or 4-dodecyloxybenzaldehyde (**8b**) [35, 36] yielded the target compounds **1a** and **1b**, respectively (Scheme 2). The nitriles **4**, **5** and **7** form colorless crystals, which can be used directly for the subsequent reaction step. Nevertheless, their purity was checked by ^{1}H NMR spectroscopy (Table 1). The portion of *Z* configuration in all compounds including **1a**, **b** was below the detection limit of 5 %.

Table 1. ^{1}H NMR spectra of the nitriles **4**, **5** and **7**; δ values [ppm] in $CDCl_3$, TMS as internal standard.

Compound	Benzonitrile moiety AA′BB′	Olefinic double bond AB	^3J (Hz)	Other benzene ring AA′BB′	Side chain
4	7.54/7.60	7.09/7.17	16.2	7.18/7.41	2.38 (s, CH_3)
5	7.53/7.62	7.08/7.17	16.2	7.39/7.41	4.50 (s, CH_2)
7	7.53/7.58	7.05/7.17	16.3	7.28/7.45	1.23 (m, CH_3) 3.12 (d, $^2J_{P,H}$ = 21.2 Hz, CH_2P) 4.00 (m, OCH_2)



Product	**1a**	**1b**
R	C_6H_{13}	$C_{12}H_{25}$
Yield **4** → **1** (%)	27	33

Scheme 2. Preparation of the push-pull-substituted (*E*,*E*)-1,4-distyrylbenzenes **1a**, **b**.

The DAOPVs **1a**, **b** (n = 2) are green-yellow solids. Their long-wavelength absorption maxima in $CHCl_3$ solution are observed at 375 nm. The push-pull effect causes a bathochromic shift compared to the parent system 1,4-distyrylbenzene, which has a λ_{max} value of 356 nm ($CHCl_3$). The polarization of these rod-like molecules can be seen by regarding the ^{13}C chemical shifts, in particular the $\Delta\delta$ values of the olefinic carbon atoms. Fig. 1 depicts the data of **1a**: $\Delta\delta = 132.1 - 126.2 = 5.9$ ppm (acceptor side), $\Delta\delta = 129.0 - 125.9 = 3.1$ ppm (donor side). Compound **1b** shows the same effect. The correlation of the signals with certain nuclei was based on INDOR, NOE and HMBC measurements.

The target compounds **1a**, **b** are thermally stable up to 320 °C. Their DSC diagrams contain between 20 and 320 °C four reversible phase transitions, which are listed in Table 2.

Cooling of the isotropic melt **I** in both cases leads first to an isotropic, non-birefringent LC phase. The light in the polarization microscope is parallel to the optical axis of these rod-like molecules. Further cooling generates smectic phases *S* at 253 and 245 °C, respectively. These phase transitions have by far the highest ΔH values. The textures of the smectic phases *S* consist of mosaic patterns with curved fissures, whose number increases on further cooling to a smectic phase *S*′ with a very low mobility. We assume the formation of higher ordered smectic phases, such as S_B.

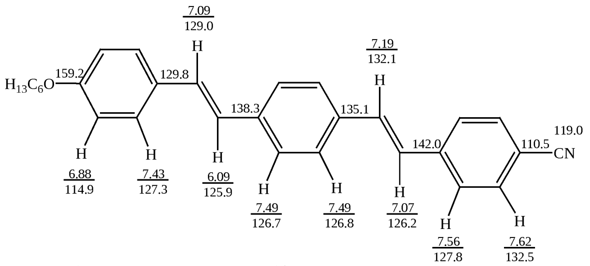


Fig. 1. ^{1}H (underlined) and ^{13}C chemical shifts of **1a** (δ values in ppm in $CDCl_3$, related to TMS as internal standard).

Recently performed small-angle X-ray scattering (SAXS) and polarized optical microscopy (POM) measurements of related compounds **1** (D = alkoxy, A = ester, n = 2) [37] demonstrated the problems to determine

Table 2. Phase transitions of compounds **1a** and **1b** between the crystalline phase **K** at room temperature and the isotropic melt **I** at 300 °C (DSC rate ± 10 K min^{-1}).

Compound		Onset transition temperature T (°C)	Transition enthalpy ΔH (kJ mol^{-1})
		K	
1a	Heating curve	176	2
		192	3
		251	19
		295	~ 1
		I	
	Cooling curve	295	~ − 1
		253	~ −16
		187	− 3
		176	~ − 1
		K	
1b	Heating curve	70	2
		164	4
		240	15
		289	5
		I	
	Cooling curve	293	− 4
		245	− 15
		163	− 4
		74	− 3

precisely the molecular arrangement of such OPVs in smectic phases. The mesophases of **1a**, **b** are photostable. The strong dipole character of these compounds should enable an efficient electrical orientation or reorientation of the molecules in switching processes. Moreover, high first-order hyperpolarizabilities (SHG) can be expected. EFISHG measurements of a related system **1** (n = 2, A = NO_2, D = NR_2), which does not form mesophases, gave a very high value $\beta_{ZZZ} = (716 \pm 31)\ 10^{-50}\ \text{C m}^3\ \text{V}^{-2}$ [38].

Conclusion

The push-pull-substituted (*E*,*E*)-1,4-distyrylbenzenes **1a**, **b** with cyano and alkoxy termini can be prepared by applying Wittig-Horner reactions. Hexyloxy or dodecyloxy groups serve as electron donors and enable the formation of smectic mesophases. The compounds are photostable and owing to their strong dipole character, they should permit an efficient electrical switching process and high hyperpolarizabilities β.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer. FD MS measurements were performed with a Finnigan MAT 95 spectrometer. The UV/Vis spectra were recorded on a Zeiss MCS 320/340 and the IR spectra on a Beckman Acculab spectrometer. A Perkin-Elmer DSC-7 instrument served for the differential scanning calorimetry. Melting points were measured with a Büchi melting point apparatus and are uncorrected. A Leitz Ortholux II microscope together with a Mettler FP-52 heating system was used for the polarization microscopy. Elemental analyses were performed in the microanalytical laboratory of the Chemistry Department of the University of Mainz.

*(E)-4-[2-(4-Methylphenyl)vinyl]benzonitrile (**4**)*

Preparation according to ref. [33]. Colorless crystals, yield 56 %, m. p. 178 °C. – ^{13}C NMR ($CDCl_3$): δ = 21.3 (CH_3), 110.3, 133.6, 138.6, 142.1 (aromat. C_q), 119.0 (CN), 125.7, 132.4 (olefin. CH), 126.7, 126.9, 129.6, 132.5 (aromat. CH).

*General procedure for the preparation of the (E,E)-4-[2-(4-{2-[4-(alkoxy)phenyl]vinyl}phenyl)vinyl]benzonitriles (**1a**, **b**)*

Nitrile **4** (6.0 g, 27.4 mmol) and *N*-bromosuccinimide (5.34 g, 30 mmol) were heated in 80 mL of CCl_4 to 40 °C. Dibenzoylperoxide (0.1 g, 0.42 mmol) was added portionwise while the mixture was refluxed for 3 h. *n*-Hexane (150 mL) was added to the hot-filtered solution. The brominated nitrile **5** crystallized overnight at 5 °C. It was then treated with triethyl phosphite **6** (4.16 g, 25 mmol) at 160 °C for 1 h. The generated bromoethane was removed continously. Distillation in the vacuum (0.1 kPa) gave first some excess phosphite (**6**) and then phosphonate **7**, a light-yellow, viscous oil, which started to crystallize at r. t. It was dissolved together with 4-alkoxybenzaldehyde **8a** or **8b** (20.0 mmol) in 50 mL of DMF and then dropped to a vigorously stirred suspension of KOH (2.8 g, 50 mmol) in 50 mL of DMF. During the addition the temperature was kept below 5 °C and then slowly raised to 50 °C. After 2 h at 50 °C, 100 mL of methanol was added. The green-yellow crystals formed at 0 °C were filtered, washed with cold methanol and purified by column filtration (4 × 10 cm SiO_2, $CHCl_3$). The total yield related to **4** amounts to 3.0 g (27 %) of **1a** and 4.4 g (33 %) of **1b**. The melting and clearing processes are discussed in the theoretical part.

*(E,E)-4-[2-(4-{2-[4-(Hexyloxy)phenyl]vinyl}phenyl)vinyl]-benzonitrile (**1a**)*

IR (KBr): ν (cm^{-1}) = 2930, 2230, 1595, 1580, 1505, 1250, 1170, 965, 835. – FD MS: m/z (%) = 408 (100) $[M]^+$. – $C_{29}H_{29}NO$ (407.56): calcd. C 85.47, H 7.17, N 3.44; found C 85.47, H 7.26, N 3.55.

*(E,E)-4-[2-(4-{2-[4-(Dodecyloxy)phenyl]vinyl}phenyl)vinyl]-benzonitrile (**1b**)*

IR (KBr): ν (cm^{-1}) = 2900, 2220, 1595, 1580, 1505, 1245, 1170, 960, 830. – ^{1}H NMR ($CDCl_3$): δ = 0.89 (m, 3H, CH_3), 1.2 – 1.4 (m, H, CH_2), 1.45 (m, 2H, CH_2), 1.78

(m, 2H, CH_2), 3.98 (t, 2H, OCH_2), 6.88/7.43 (AA′BB′, 4H, aromat. H, donor side), 6.09/7.09 (AB, ^3J = 16.2 Hz, 2H, olefin. H, donor side), 7.07/7.19 (AB, ^3J = 16.2 Hz, 2H, olefin. H, acceptor side), 7.49 (m, 4H, aromat. H, middle), 7.56/7.62 (AA′BB′, 4H, aromat. H, acceptor side). – ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.1, 29.3, 29.4, 29.6, 29.7, 31.9 (CH_2, partly superimposed), 68.2 (OCH_2), 114.6, 126.7, 126.8, 127.3, 127.8, 132.5 (aromat. CH), 125.8, 126.3, 129.0, 132.1 (olefin. CH), 110.5, 129.8, 135.2, 138.3, 142.0 (aromat. C_q), 119.1 (CN), 159.2 (aromat. C_qO).

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