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Synthesis and Structural Studies of Poly(*p*-phenylenevinylene) Analogous Model Compounds

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Described is the synthesis and characterization of three poly(*p*-phenylenevinylene) (PPV) three-ring model compounds, one unsubstituted at the vinylene moiety (**1**) and two dicyano-substituted compounds (**2**, **3**), differing in the positions of their cyano groups. Single-crystal analyses of the two cyano-substituted compounds **2** and **3** show that introduction of cyano groups into alkyl-substituted PPV analogous compounds leads to remarkable torsion of the conjugated backbones unlike hexyloxy-substituted compounds. In the case of introducing it into the α-position as in **2**, the torsion is distributed almost equally over the molecule. Introducing the cyano group into the β-position as in **3** leads to a one-sided torsion between the inner phenylene ring and the vinylene−CN planes.

Introduction

Since the detection of light emission from poly(*p*-phenylenevinylene) (PPV)[1] and PPV analogous polymers,[2−4] the interest in this class of compounds has greatly emerged. Substitution of the PPV backbone increases solubility and thus processability of the polymers and allows one to change the electronic and optical properties in almost every desired direction. To understand the mechanisms of light emission and to predict the influences of substitution on the emitted light, model compounds such as short oligomers or well-defined sections of PPV have been synthesized and their properties have been examined.[4−12] These short-chain model compounds allow study of the influences of substituents on the absorption and emission characteristics. Substituents in the PPV core could affect the electronic and optical behavior of the molecules first because of their electron-donating or -accepting characters and second because of steric reasons such as deformation of the conjugated backbone. A useful tool to predict steric influences is the single-crystal X-ray analysis of model compounds. Another advantage of this technique is the possibility to get an insight into packing of the molecules and structural organization of the related polymers and thus a help to explain the mechanisms of luminescence phenomena. Although, however, these structure−property relationships are of fundamental interest, only a few single-crystal structural analyses of PPV analogous model compounds have been reported.[5−8]

In this paper we describe the crystal structures of two hexyl-substituted PPV analogous model compounds (**2** and **3** in Figure 1) and outline the steric influences of the introduction of cyano groups.

Experimental Section

Measurements. NMR spectra were recorded on a Bruker AC 250 spectrometer at 250 MHz (^{1}H) and 62.9 MHz (^{13}C) in $CDCl_3$ and internally referenced to $CHCl_3$ (^{1}H: $\delta = 7.24$ ppm, ^{13}C: $\delta = 77.00$ ppm). Elemental analyses (EA) were carried out on a Carlo Erba Elemental Analyzer 1106. IR spectra were recorded as KBr pellets on a Bruker IFS 48 spectrometer.

Materials. Commercially available chemicals (Aldrich and Fluka) were used without further purification. Diethyl ether and ethanol were dried over sodium, tetrahydrofuran was dried over calcium hydride, and chloroform was dried over $CaCl_2$, and all were distilled before use. 2,5-Di-*n*-hexylterephthalonitrile,[13] benzyl triphenylphosphonium bromide,[14] 2,5-biscyanomethyl-1,4-di-*n*-hexylbenzene, and the bis(styryl)benzenes[4] **2** and **3** were prepared according to literature

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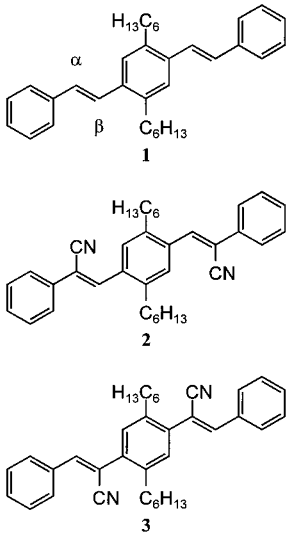

1

2

3

Figure 1. Chemical structures of 1,4-bisstyryl-2,5-di-*n*-hexylbenzene **1**, 1,4-bis(α-cyanostyryl)-2,5-di-*n*-hexylbenzene **2**, and 1,4-bis(*β*-cyanostyryl)-2,5-di-*n*-hexylbenzene **3**.

procedures. All reactions were performed under a dry nitrogen atmosphere.

2,5-Di-*n*-hexylterephthalaldehyde. To an ice-cooled solution of 10 g (33.1 mmol) of 2,5-di-*n*-hexylterephthalonitrile in 400 mL dry diethyl ether is added 50 mL (75 mmol) of a 1.5 M solution of diisobutylaluminumhydride (DIBAL-H) in toluene. The ice bath is removed, and the mixture is allowed to reflux. After a short time a yellow jelly-like substance is formed. The mixture is kept under reflux for 2 d. The ice-cooled reaction mixture is then quenched carefully with methanol (ca. 20 mL) followed by water (ca. 50 mL) and 2 M hydrochloric acid (ca. 200 mL). Finally concentrated HCl is added during 1 h until the white deposit is complete dissolved. The aqueous layer is separated and extracted twice with diethyl ether. The combined organic layers are washed successively with water, saturated $NaHCO_3$ solution, and again with water and then are dried over $MgSO_4$. After removal of the solvent, the yellow oil is purified by flash chromatography with silica gel and a *n*-hexane/CH_2Cl_2 (7:3) mixture. The solvent is evaporated and the residue is dried at 0.05 mbar. Yield: 9.2 g, 90%; mp 53−54 °C. ^{1}H NMR: 0.85 (t, $J = 6.9$ Hz), 1.29 (m), 1.59 (m), 3.00 (t, $J = 7.8$ Hz), 7.70 (s), 10.32 (s) ppm. ^{13}C NMR: 13.98, 22.50, 29.10, 31.54, 31.78, 32.27, 133.07, 136.73, 143.34, 191.62 ppm. IR: 2957 (s), 2924 (s), 2852 (m), 1686 (s), 1466 (m), 1400 (m) cm^{-1}.

1,4-Bisstyryl-2,5-di-*n*-hexylbenzene 1. To a suspension of 0.5 g (1.66 mmol) of 2,5-di-*n*-hexylterephthalaldehyde and 1.5 g (3.46 mmol) of benzyl triphenylphosphonium bromide in 10 mL of dry chloroform is added dropwise a solution of 0.5 g of sodium in 20 mL dry ethanol. The mixture is stirred for 4 h at ambient temperature, and subsequently 5% HCl is added until the precipitate is dissolved. The organic phase is separated, and the aqueous phase is extracted twice with dichloromethane. The combined organic phases are dried over $CaCl_2$ and evaporated. The crude product is dissolved in toluene, a catalytic amount of I_2 is added, and the mixture is heated 3 h under reflux in order to obtain pure trans isomers. After evaporation of the solvent, the crude product is purified first by column chromatography with silica gel and then by reprecipitation from dichloromethane solution with methanol. Yield: 249 mg, 33%; mp 85−86 °C. ^{1}H NMR: 0.90 (t, $J = 6.9$ Hz), 1.46−1.26 (m), 1.70−1.57 (m), 2.76 (t, $J = 7.8$ Hz), 7.03 (d, $J = 16.1$ Hz), 7.37 (d, $J = 16.1$ Hz), 7.41−7.25 (m), 7.44 (s), 7.55−7.52 (m) ppm. ^{13}C NMR: 14.10, 22.65, 29.34, 31.38, 31.72, 33.28, 126.11, 126.50, 126.72, 127.46, 128.68, 129.39, 135.02, 137.88, 138.56 ppm. IR: 2959 (s), 2930 (s), 2858 (s), 1605 (w), 1529 (w), 1501 (m), 1468 (m), 1364 (s), 1209 (s), 1119 (s) cm^{-1}. EA calcd: C, 90.61; H, 9.39. Found: C, 89.96; H, 9.97.

Table 1. Crystallographic and Experimental Data of Compounds 2 and 3

	2	3
	Crystal Data	
formula	$C_{36}H_{40}N_2$	$C_{36}H_{40}N_2$
formula wt (g/mol)	500.7	500.7
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	12.383(2)	11.257(3)
b (Å)	11.6487(10)	11.4020(13)
c (Å)	20.879(4)	12.257(2)
α (deg)	90	90
β (deg)	100.015(9)	110.493(8)
γ (deg)	90	90
V (Å^3)	2965.8(8)	1473.7(5)
Z	4	2
D_{calc} (g/cm^{-3})	1.121	1.128
F(000)	1080	540
μ (Cu Kα) (cm^{-1})	4.87	4.90
crystal size (mm^3)	0.90 × 0.25 × 0.20	0.60 × 0.40 × 0.30
	Data Collection	
T (K)	213(2)	213(2)
Θ range; min, max (deg)	5.12, 64.89	5.47, 65.17
reflns collected	5810	4838
independent reflns	5044	2515
no. of reflns observed ($I > 2\sigma(I)$)	3967	2049
	Structure and Refinement	
no. of parameters	335	194
R_1 ($I > 2\sigma(I)$)	0.0812	0.0817
wR_2 ($I > 2\sigma(I)$)	0.2237	0.2438
R_1 (all)	0.0983	0.0920
wR_2 (all)	0.2408	0.2618

1,4-Bis(α-cyanostyryl)-2,5-di-*n*-hexylbenzene 2. Yield: 88%; mp 119−120 °C. ^{1}H NMR: 0.85 (t, $J = 6.95$ Hz), 1.43−1.25 (m), 1.70−1.58 (m), 2.73 (t, $J = 7.74$ Hz), 7.51−7.41 (m), 7.69 (dd, $J = 1.56$ Hz, 7.83 Hz), 7.79 (s), 7.85 (s) ppm. ^{13}C NMR: 13.99, 22.52, 29.05, 30.95, 31.61, 33.19, 114.46 117.60, 126.11, 129.13, 129.42, 134.23, 134.28, 140.20, 140.38 ppm. IR: 3063 (m), 3028 (m), 2957 (s), 2922 (s), 2874 (s), 2850 (s), 2362 (m), 2214 (s), 1589 (m), 1497 (m), 1466 (m), 1448 (m), 912 (s), 758 (s), 731 (m), 690 (s) cm^{-1}. EA calcd: C, 86.35; H, 8.05; N, 5.59. Found: C, 86.55; H, 7.76; N, 5.65.

1,4-Bis(*β*-cyanostyryl)-2,5-di-*n*-hexylbenzene 3. Yield: 70%; mp 111−112 °C. ^{1}H NMR: 0.84 (t, $J = 6.96$ Hz), 1.39−1.24 (m), 1.71−1.59 (m), 2.78 (t, $J = 7.96$ Hz), 7.14 (s), 7.19 (s), 7.52−7.45 (m), 7.91−7.86 (m) ppm. ^{13}C NMR: 13.98, 22.52, 29.23, 30.84, 31.54, 32.64, 110.46, 117.99, 129.00, 129.12, 130.75, 131.03, 133.49, 136.06, 139.34, 147.17 ppm. IR: 3055 (w), 3026 (w), 2959 (m), 2922 (s), 2853 (s), 2208 (s), 1600 (m), 1573 (w), 1497 (m), 1464 (m), 1448 (m), 1358 (m), 1186 (m), 931 (w), 920 (m), 897 (m), 750 (m), 685 (s), 628 (w) cm^{-1}. EA calcd: C, 86.35; H, 8.05; N, 5.59. Found: C, 86.00; H, 8.23; N, 5.63.

X-ray Diffraction. Data collection was performed using graphite-monochromatized Cu Kα radiation ($\lambda = 1.54184$ Å) on a Nonius CAD4 diffractometer. The intensities of three standard reflections, which were measured every hour, showed no greater fluctuations during data collection than those expected from Poisson statistics. Neutral atom scattering factors and anomalous dispersion corrections were taken from International Tables of Crystallography.[15]

Single crystals were grown from dichloromethane/*n*-hexane solution (**2**) and chloroform/*n*-hexane solution (**3**). The crystals were mounted onto the top of a glass fiber and transferred into the cold nitrogen stream of the low-temperature unit. Cell

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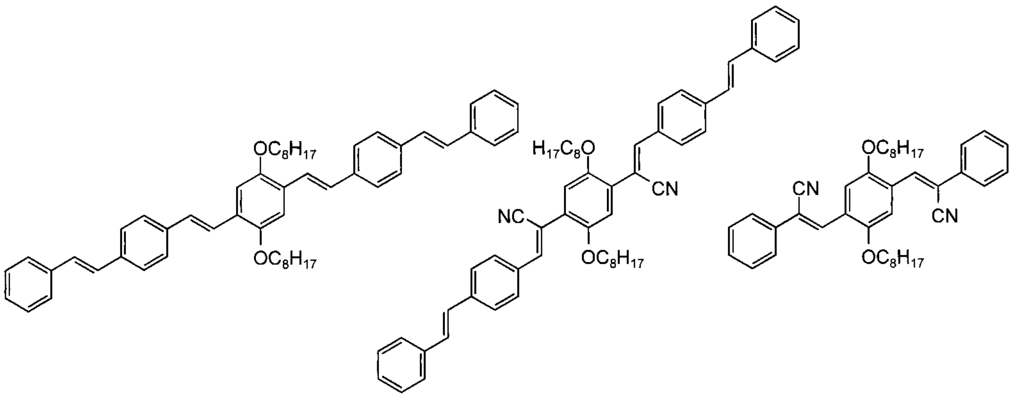

4 **5** **6**

Figure 2. PPV analogous model compounds of which the X-ray structures have been described.[6-8]

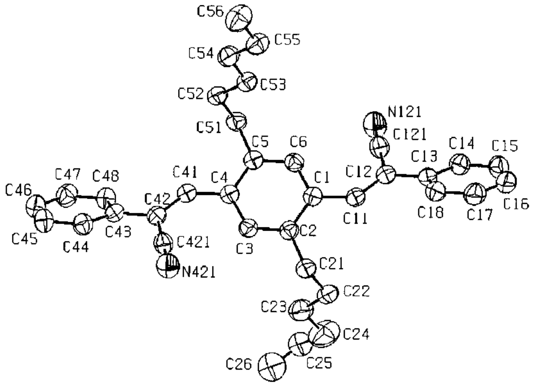

Figure 3. ORTEP plot of the non-hydrogen atoms and labeling scheme of **2**.

Table 2. Photoluminescence and Absorption Maxima

compd	UV_{max} [nm]	PL_{max} (solution)	PL_{max} (film)
1	342	418/396	445[a]/465
2	351	455	470[a]/495[b]
3	300	408	420

[a] Main peak. [b] Shoulder.

constants and an orientation matrix for the data collection were obtained from a least-squares refinement of 25 reflections in the ranges of $5.12° < \Theta < 64.89°$ (**2**) and $5.47° < \Theta < 65.17°$ (**2**), respectively. The structure was solved by direct methods with SHELXS-86.[16] Crystal data and additional experimental data are given in Table 1. The positional and anisotropic thermal displacement parameters for the non hydrogen atoms were refined with full-matrix least-squares procedures.[17] A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms, the coordinates and isotropic thermal displacement parameters of which were refined. Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $R_1 = 0.0812$ for 3967 reflections with $I > 2\sigma(I)$ and 335 parameters for compound **1** and $R_1 = 0.0817$ for 2049 reflections with $I > 2\sigma(I)$ and 194 parameters for compound **2**. The final difference maps showed no unusual features, with no significant peak having chemical meaning above the general background.

Results and Discussion

According to theoretical calculations[18,19] and experimental data,[10,11] introduction of cyano groups in the vinylene moieties of PPV analogous compounds should lead to a red shift of the absorption and emission data. Table 2 gives the values of UV absorption and photoluminescence (PL) emission maxima of 1,4-bisstyryl-2,5-di-*n*-hexylbenzene **1** and the two cyano-substituted analogues 1,4-bis(α-cyanostyryl)-2,5-di-*n*-hexylbenzene **2** and 1,4-bis(β-cyanostyryl)-2,5-di-*n*-hexylbenzene **3**. Introduction of cyano substituents at the α-position of the styryl moieties of **1** forming compound **2** confirms the expected bathochromic shift. If the cyano groups are introduced at the β-positions of the vinylene group forming **3**, however, the maxima of PL and absorption are significantly blue shifted. This effect can be explained with steric reasons: moving the cyano groups next to the hexyl chains causes deformation and thus a shortening of the conjugation length of the molecule, resulting in the observed hypsochromic shift. To prove this assumption, single crystals of **2** and **3** have been grown which were appropriate for an X-ray diffraction experiment.

Comparable molecules **4**–**6** (Figure 2) that have already been examined by single-crystal X-ray analyses carry octyloxy chains at their central phenylene rings.[6-8] In these molecules, the angles between the central phenylene rings and the (CN–)vinylene planes are relatively small. Introducing the cyano groups into the inner β-positions (compound **5)** causes an almost 180° rotation around the single bonds next to the central phenylene ring, leading again to an almost planar arrangement.[6] Thus in the case of compounds **5** and **6**, the cyano groups are virtually in the planes of the central phenylene rings. Substituting the oxyalkyl groups by alkyl groups (hexyl groups) as in **2** and **3**, however, causes a remarkable torsion of the conjugated backbone.

Crystal Structure of 2. Experimental data are given in Table 1. The compound crystallizes in a monoclinic unit cell containing four discrete molecules. The spacegroup is $P2_1/c$. The conformation of the molecule and the labeling scheme of the atoms are shown in Figure 3. The molecule is remarkably twisted. The angle of the plane formed by the carbons C11, C12, C121 relative to the plane of the central phenylene ring (C1, C2, C3, C4) is 27.56°, and the similar angle with

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Table 3. Full Bond Lengths and Angles for 2 (Standard Deviations in the Last Decimal Place Are Given in Parentheses)

Bond Lengths (Å)

N(121)−C(121)	1.148(4)	C(17)−C(18)	1.380(4)
N(421)−C(421)	1.147(3)	C(21)−C(22)	1.533(4)
C(1)−C(6)	1.390(3)	C(22)−C(23)	1.518(4)
C(1)−C(2)	1.417(3)	C(23)−C(24)	1.532(5)
C(1)−C(11)	1.463(3)	C(24)−C(25)	1.605(8)
C(2)−C(3)	1.391(3)	C(25)−C(26)	1.252(9)
C(2)−C(21)	1.504(3)	C(41)−C(42)	1.353(4)
C(3)−C(4)	1.394(3)	C(42)−C(421)	1.443(4)
C(4)−C(5)	1.419(3)	C(42)−C(43)	1.480(3)
C(4)−C(41)	1.463(3)	C(43)−C(44)	1.391(4)
C(5)−C(6)	1.388(3)	C(43)−C(48)	1.396(4)
C(5)−C(51)	1.503(3)	C(44)−C(45)	1.382(4)
C(11)−C(12)	1.357(4)	C(45)−C(46)	1.370(5)
C(12)−C(121)	1.436(4)	C(46)−C(47)	1.378(5)
C(12)−C(13)	1.482(3)	C(47)−C(48)	1.382(4)
C(13)−C(18)	1.394(4)	C(51)−C(52)	1.537(4)
C(13)−C(14)	1.398(4)	C(52)−C(53)	1.523(4)
C(14)−C(15)	1.386(4)	C(53)−C(54)	1.514(4)
C(15)−C(16)	1.369(5)	C(54)−C(55)	1.513(4)
C(16)−C(17)	1.383(5)	C(55)−C(56)	1.507(4)

Bond Angles (deg)

C(6)−C(1)−C(2)	118.6(2)	C(17)−C(18)−C(13)	120.3(3)
C(6)−C(1)−C(11)	122.1(2)	C(2)−C(21)−C(22)	114.1(2)
C(2)−C(1)−C(11)	119.3(2)	C(23)−C(22)−C(21)	114.0(2)
C(3)−C(2)−C(1)	117.6(2)	C(22)−C(23)−C(24)	112.9(3)
C(3)−C(2)−C(21)	119.0(2)	C(23)−C(24)−C(25)	116.4(4)
C(1)−C(2)−C(21)	123.3(2)	C(26)−C(25)−C(24)	108.2(8)
C(2)−C(3)−C(4)	123.8(2)	C(42)−C(41)−C(4)	130.0(2)
C(3)−C(4)−C(5)	118.4(2)	C(41)−C(42)−C(421)	121.5(2)
C(3)−C(4)−C(41)	122.0(2)	C(41)−C(42)−C(43)	123.1(2)
C(5)−C(4)−C(41)	119.5(2)	C(421)−C(42)−C(43)	115.3(2)
C(6)−C(5)−C(4)	117.7(2)	C(44)−C(43)−C(48)	118.6(2)
C(6)−C(5)−C(51)	119.0(2)	C(44)−C(43)−C(42)	121.0(2)
C(4)−C(5)−C(51)	123.3(2)	C(48)−C(43)−C(42)	120.4(2)
C(5)−C(6)−C(1)	123.9(2)	C(45)−C(44)−C(43)	120.4(3)
C(12)−C(11)−C(1)	129.5(2)	C(46)−C(45)−C(44)	120.5(3)
C(11)−C(12)−C(121)	121.7(2)	C(45)−C(46)−C(47)	120.0(3)
C(11)−C(12)−C(13)	122.9(2)	C(46)−C(47)−C(48)	120.2(3)
C(121)−C(12)−C(13)	115.5(2)	C(47)−C(48)−C(43)	120.3(3)
C(18)−C(13)−C(14)	118.7(2)	C(5)−C(51)−C(52)	113.5(2)
C(18)−C(13)−C(12)	120.5(2)	C(53)−C(52)−C(51)	113.4(2)
C(14)−C(13)−C(12)	120.8(2)	C(54)−C(53)−C(52)	114.2(2)
C(15)−C(14)−C(13)	120.1(3)	C(55)−C(54)−C(53)	114.2(2)
C(16)−C(15)−C(14)	120.5(3)	C(56)−C(55)−C(54)	113.6(3)
C(15)−C(16)−C(17)	120.0(3)	N(121)−C(121)−C(12)	178.4(3)
C(18)−C(17)−C(16)	120.3(3)	N(421)−C(421)−C(42)	178.4(3)

Selected Torsion Angles (deg)

C(6)−C(1)−C(11)−C(12)	23.8	C(3)−C(4)−C(41)−C(42)	−23.5
C(11)−C(12)−C(13)−C(18)	22.6	C(41)−C(42)−C(43)−C(48)	−23.9
C(121)−C(12)−C(13)−C(14)	20.8	C(421)−C(42)−C(43)−C(44)	−22.1
C(1)−C(11)−C(12)−C(121)	6.4	C(4)−C(41)−C(42)−C(421)	−6.4

Table 4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\times 10^3$ Å^2) for 2

	x	y	z	U_{eq}[a]
N(121)	1.0423(2)	−0.2747(2)	0.8035(1)	66(1)
N(421)	0.4623(2)	0.2205(2)	0.6902(1)	62(1)
C(1)	0.8504(2)	−0.0398(2)	0.7222(1)	40(1)
C(2)	0.7564(2)	0.0066(2)	0.6822(1)	40(1)
C(3)	0.6609(2)	0.0157(2)	0.7084(1)	42(1)
C(4)	0.6537(2)	−0.0152(2)	0.7720(1)	39(1)
C(5)	0.7480(2)	−0.0617(2)	0.8120(1)	40(1)
C(6)	0.8430(2)	−0.0713(2)	0.7855(1)	41(1)
C(11)	0.9530(2)	−0.0486(2)	0.6968(1)	40(1)
C(12)	1.0412(2)	−0.1169(2)	0.7164(1)	40(1)
C(13)	1.1435(2)	−0.1087(2)	0.6889(1)	41(1)
C(14)	1.2162(2)	−0.2012(3)	0.6929(1)	51(1)
C(15)	1.3109(2)	−0.1927(3)	0.6663(2)	62(1)
C(16)	1.3342(2)	−0.0939(3)	0.6359(2)	64(1)
C(17)	1.2641(2)	−0.0009(3)	0.6327(2)	60(1)
C(18)	1.1696(2)	−0.0077(3)	0.6591(1)	49(1)
C(21)	0.7546(2)	0.0438(3)	0.6130(1)	49(1)
C(22)	0.7476(2)	−0.0557(3)	0.5644(1)	56(1)
C(23)	0.6414(3)	−0.1234(3)	0.5571(2)	67(1)
C(24)	0.6388(4)	−0.2255(4)	0.5107(2)	98(1)
C(25)	0.5418(6)	−0.3168(7)	0.5110(4)	167(3)
C(26)	0.4525(7)	−0.2675(8)	0.4910(4)	193(3)
C(41)	0.5515(2)	−0.0047(2)	0.7977(1)	40(1)
C(42)	0.4635(2)	0.0637(2)	0.7783(1)	40(1)
C(43)	0.3620(2)	0.0575(2)	0.8066(1)	42(1)
C(44)	0.2915(2)	0.1510(3)	0.8039(1)	52(1)
C(45)	0.1982(2)	0.1446(3)	0.8316(2)	62(1)
C(46)	0.1734(3)	0.0459(3)	0.8616(2)	63(1)
C(47)	0.2409(2)	−0.0486(3)	0.8635(2)	58(1)
C(48)	0.3348(2)	−0.0434(2)	0.8362(1)	49(1)
C(51)	0.7510(2)	−0.0954(2)	0.8817(1)	44(1)
C(52)	0.7655(2)	0.0069(2)	0.9289(1)	48(1)
C(53)	0.8741(2)	0.0695(2)	0.9313(1)	47(1)
C(54)	0.8900(2)	0.1708(3)	0.9775(1)	53(1)
C(55)	0.9956(2)	0.2361(3)	0.9776(1)	56(1)
C(56)	1.0106(3)	0.3361(3)	1.0240(2)	77(1)
C(121)	1.0405(2)	−0.2041(2)	0.7650(1)	47(1)
C(421)	0.4640(2)	0.1505(2)	0.7290(1)	47(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

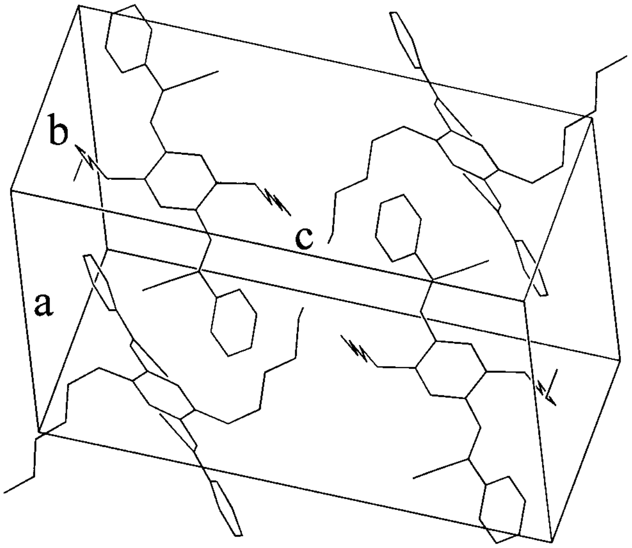


Figure 4. Unit cell of **2** viewed perpendicular to the *c* axis.

C41, C42, C421 is almost the same (27.06°). The outer phenylene rings are twisted 48.32° (C13, C14, C15) and 49.12° (C43, C44, C48) relative to the inner one. Since the dihedral angles across the single bonds on the two sides of this inner ring have opposite signs, the outer phenylene rings are almost coplanar. All bond angles and bond lengths are in the normal range. The values are given in Table 3. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table 4.

Packing of the molecules of **2** seems to be greatly affected by the hexyl chains. One hexyl chain of each molecule is pointing in toward the unit cell (Figure 4), thus their terminal methyl groups form the edges of a parallelogram whose center is the same as the center of the unit cell. Figure 5a shows two molecules in neighboring unit cells, related by a translation along the *a* axis. The four marked atoms are virtually in plane. The inticated distance of 3.6 Å is the shortest distance occurring between two molecules in the crystal, however, somewhat too large for intense π−π interaction.

Crystal Structure of 3. Experimental data are given in Table 1. The compound also crystallizes in a monoclinic unit cell with the spacegroup $P2_1/c$. The conformation and the labeling scheme are shown in

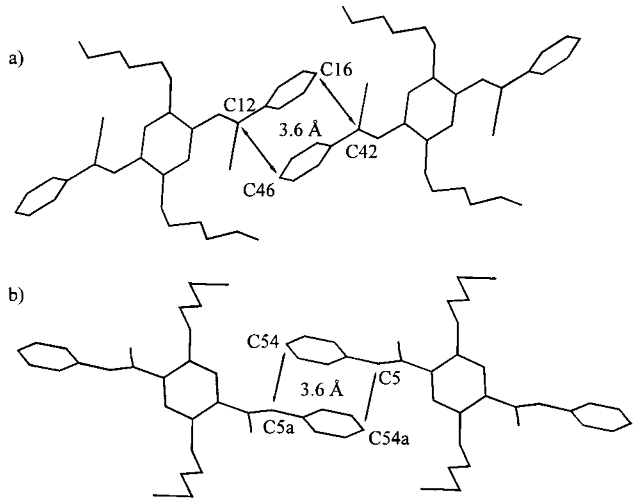


Figure 5. Arrangement of two molecules of **2** (a) and **3** (b) in neighboring unit cells, related by translations along the *a* axis (a) and the *c* axis (b), respectively.

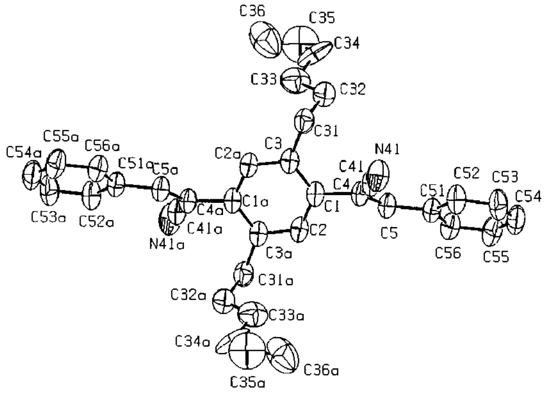


Figure 6. ORTEP plot of the non-hydrogen atoms and labeling scheme of **3**.

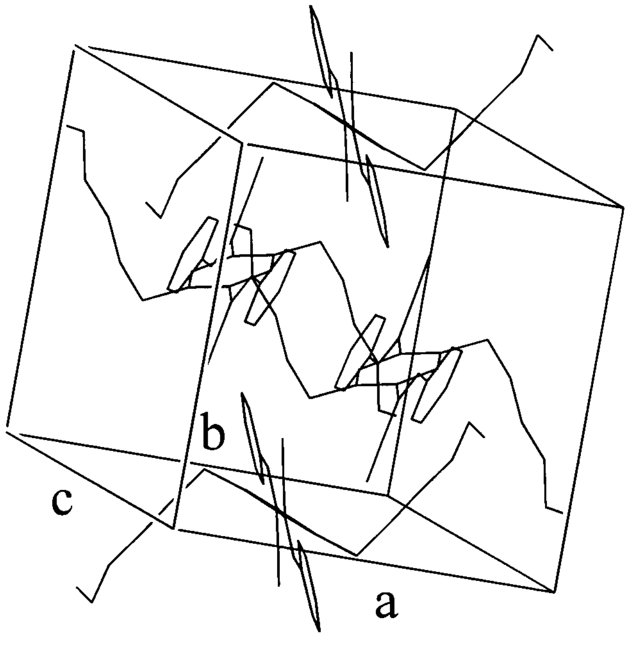


Figure 7. Unit cell of **3** viewed perpendicular to the *a* axis.

Figure 6. In case of **3** the unit cell (Figure 7) contains only two discrete molecules.

Table 5. Full Bond Lengths and Angles for 3 (Standard Deviations in the Last Decimal Place Are Given in Parentheses)

Bond Lengths (Å)			
C(1)−C(3)[a]	1.394(2)	C(34)−C(35)	1.428(5)
C(1)−C(2)	1.401(2)	C(35)−C(36)	1.369(5)
C(1)−C(4)	1.498(2)	C(41)−N(41)	1.146(2)
C(2)−C(3)	1.400(2)	C(51)−C(56)	1.387(2)
C(3)−C(1)	1.394(2)	C(51)−C(52)	1.393(2)
C(3)−C(31)	1.509(2)	C(52)−C(53)	1.381(2)
C(4)−C(5)	1.336(2)	C(53)−C(54)	1.373(3)
C(4)−C(41)	1.440(2)	C(54)−C(55)	1.371(2)
C(5)−C(51)	1.465(2)	C(55)−C(56)	1.379(2)
C(31)−C(32)	1.521(2)	C(32D)−C(33D)[b]	1.90(2)
C(31)−C(32D)	2.04(2)	C(33D)−C(34D)	1.40(2)
C(32)−C(33)	1.542(3)	C(34D)−C(35D)	1.447(13)
C(33)−C(34)	1.561(3)	C(35D)−C(36D)	1.571(9)
Bond Angles (deg)			
C(3)[a]−C(1)−C(2)	119.87(11)	C(35)−C(34)−C(33)	122.0(3)
C(3)−C(1)−C(4)	123.36(12)	C(36)−C(35)−C(34)	111.0(3)
C(2)−C(1)−C(4)	116.77(13)	N(41)−C(41)−C(4)	176.23(14)
C(3)−C(2)−C(1)	122.70(14)	C(56)−C(51)−C(52)	117.98(13)
C(1)−C(3)−C(2)	117.42(13)	C(56)−C(51)−C(5)	116.83(12)
C(1)−C(3)−C(31)	124.19(11)	C(52)−C(51)−C(5)	125.19(13)
C(2)−C(3)−C(31)	118.21(14)	C(53)−C(52)−C(51)	120.4(2)
C(5)−C(4)−C(41)	122.66(12)	C(54)−C(53)−C(52)	120.6(2)
C(5)−C(4)−C(1)	121.91(11)	C(55)−C(54)−C(53)	119.8(2)
C(41)−C(4)−C(1)	115.18(11)	C(54)−C(55)−C(56)	119.9(2)
C(4)−C(5)−C(51)	132.64(12)	C(55)−C(56)−C(51)	121.32(14)
C(3)−C(31)−C(32)	113.76(12)	C(34D)−C(33D)−C(32D)	64.7(9)
C(31)−C(32)−C(33)	113.55(13)	C(33D)−C(34D)−C(35D)	113.9(9)
C(32)−C(33)−C(34)	111.0(2)	C(34D)−C(35D)−C(36D)	122.8(6)
Selected Torsion Angles (deg)			
C(2)−C(1)−C(4)−C(5)	47.6	C(2a)−C(1a)−C(4a)−C(5a)	−47.6
C(3a)−C(1)−C(4)−C(41)	53.3	C(3)−C(1a)−(C4a)−C(41a)	−53.3
C(4)−C(5)−C(51)−C(52)	−4.6	C(4a)−C(5a)−C(51a)−C(52a)	4.6
C(41)−C(4)−C(5)−C(51)	−2.6	C(41a)−C(4a)−C(5a)−C(51a)	2.6

[a] Symmetry transformation to generate equivalent atoms: $-x + 1, -y, -z + 1$, indicated as “a”. [b] D = disordered atoms of the hexyl chain.

Table 6. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\times 10^3$ Å^2) for 3

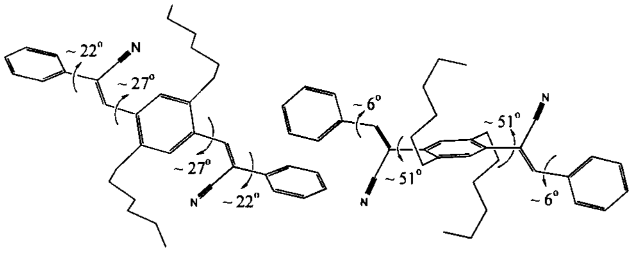
	x	y	z	U_{eq} (Å^2)
C(1)	0.5547(1)	−0.0181(1)	0.6203(1)	46(1)
C(2)	0.4331(1)	0.0300(1)	0.5700(1)	48(1)
C(3)	0.3765(1)	0.0498(1)	0.4502(1)	48(1)
C(4)	0.6037(1)	−0.0327(1)	0.7499(1)	46(1)
C(5)	0.5968(1)	0.0535(1)	0.8213(1)	49(1)
C(31)	0.2419(1)	0.0946(1)	0.4046(1)	55(1)
C(32)	0.1435(2)	−0.0008(2)	0.3538(1)	51(1)
C(33)	0.1364(2)	−0.0917(2)	0.4444(2)	65(1)
C(34)	0.0336(3)	−0.1867(2)	0.3870(3)	102(1)
C(35)	0.0334(3)	−0.2979(3)	0.4403(3)	133(2)
C(36)	0.0411(4)	−0.2850(3)	0.5536(3)	122(1)
C(41)	0.6473(1)	−0.1489(1)	0.7908(1)	52(1)
C(51)	0.6312(1)	0.0600(1)	0.9480(1)	49(1)
C(52)	0.6905(2)	−0.0288(1)	1.0261(1)	64(1)
C(53)	0.7198(2)	−0.0128(2)	1.1443(1)	73(1)
C(54)	0.6924(2)	0.0913(2)	1.1867(1)	73(1)
C(55)	0.6333(2)	0.1794(2)	1.1111(1)	72(1)
C(56)	0.6030(2)	0.1638(1)	0.9928(1)	60(1)
N(41)	0.6779(2)	−0.2436(1)	0.8174(1)	69(1)
C(32D)	0.1525(19)	−0.0627(17)	0.3917(18)	142(7)
C(33D)	0.1213(9)	−0.2250(9)	0.3608(9)	90(2)
C(34D)	0.0697(9)	−0.1770(9)	0.4393(9)	64(2)
C(35D)	0.0606(6)	−0.2591(6)	0.5260(6)	32(1)
C(36D)	−0.0077(6)	−0.3810(5)	0.4936(5)	33(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The molecule is centrosymmetric, implying coplanarity of the outer phenylene rings. The angle between the planes of the inner phenylene ring (C1, C2, C3) and the plane of C5, C4, C41 is 51.3° while the plane of the outer phenylene ring (C51, C52, C53) is twisted 6° in the opposite direction compared to the plane of C5, C4, C41, resulting in an angle between the planes of inner and outer phenylene rings of about 45°. The hexyl chains are highly disordered. All bond angles and bond lengths are in normal range. The values are given in Table 5. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table 6.

As in the case of **2**, the molecules of **3** are kept in distance by the hexyl chains. The arrangement of the two molecules of neighboring unit cells, related by translation along the *c* axis (Figure 5b), strongly resembles the arrangement of the molecules in the crystals of **2**. Like there, the four marked atoms are virtually in plane, and the shortest distance observed is 3.6 Å.

Comparison of the Crystal Structures of 2 and 3. The two 1,4-bis(cyanostyryl) compounds **2** and **3** (Figure 1) differ only in the positions of their cyano groups. In the case of **2** the cyano groups are located in α-position and in the case of **3** in the *β*-position relative to the styryl unit. The X-ray structures show that in **2** the torsion angles between the plane of the inner dihexyl-substituted phenylene ring and the vinylene units on one hand, and the torsion angles between the vinylene units and the outer phenylene rings on the other hand, are approximately the same (Figure 8). In the *β*-biscyanostyryl compound **3**, however, the angles between the inner dihexyl-substituted phenylene ring and the cyano−vinylene planes are over 51°, the outer phenylene rings are again twisted 6° in opposite direction against the cyano−vinylene planes (Figure 8). Moving the cyano group from the α- to *β*-position obviously causes a strong steric interaction with the hexyl chains, particularly with the first CH_2 unit, leading to quite a strong deviation from the planar arrangement. Due to the induced strong torsion of 51° in **3**, the conjugation length is shortened in comparison to **2**, leading to the observed hypsochromic shift of the PL and UV data as given in Table 2. This leads to the conclusion that alkoxy substituents at the phenylene units cause less steric interaction with the CN groups in the vinylene units and thereby a lesser influence on the conjugation length than alkyl groups.



2 **3**

Figure 8. Approximate torsion angles of the CN−vinylene planes relative to the plane of the central phenylene rings and of the outer phenylene rings relative to the CN−vinylene planes of **2** and **3**. Notice, these are not the proper torsion angles between four neighboring atoms, which are listed in Tables 3 and 5.

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