Synthesis and Crystal Structure of a Cyano-Substituted Oligo(*p*-phenylenevinylene)

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Received February 15, 1996[⊗]

Described is the synthesis and the single-crystal structure of an all-trans dicyano-substituted five-ring PPV oligomer having two *n*-octyloxy side chains attached onto the central phenyl ring. The crystal density ($D_{\mathrm{calc}} = 1.210$ g cm^{-3}) appears to be almost 10% higher than that of the crystalline phase of the analogue without cyano substituents. This indicates the presence of considerable packing forces, which is reflected in a remarkable "wavelike" deformation from planarity of the conjugated backbone and the stretching of the *n*-octyloxy side chains along the backbone. We attribute this dense packing to a large Coulomb interaction between neighbor molecules as a result of cyano substitution. Our results suggest that such intermolecular interactions play an important role with respect to the molecular geometry and packing in the solid state of cyano-substituted PPV-based materials.

Introduction

Poly(*p*-phenylenevinylene) (PPV) is one of the most extensively studied π-conjugated organic materials because of its promising potential for the fabrication of polymeric light-emitting diodes.[1,2] The introduction of various alkyl or alkoxy side-chain substituents[3] or the interruption of π-conjugation along the polymer backbone by means of copolymerization[3−5] provides soluble and therefore processable materials and allows tunability of the emission properties. Recently the attachment of electron-withdrawing cyano groups onto the vinylene segments resulted in red-light-emitting polymers with increased electron affinity, which drastically improved the quantum yields of luminescence in multilayer LED devices.[6,7]

Optical and electrical properties of thin films of conjugated materials are known to be strongly dependent on the coplanarity of the conjugated π-system and on the interchain distance of conjugated segments. Knowledge of the influence of substituents on these structural features is believed to be essential in order to achieve a detailed understanding of structure/property relationships in conjugated polymer materials. The study of well-defined conjugated oligomers therefore attracts increased attention since, in several cases, single crystals[8−10] or well-oriented thin films[11] can be obtained. Furthermore, structural data such as bond lengths and torsion angles can be used to verify assumptions concerning molecular geometry as well as results of quantum-chemical optimizations presented in studies of the electronic and structure-related properties of conjugated oligomers and polymers.[12,13] For instance, a coplanar arrangement of phenylene and vinylene segments is sometimes taken as a starting point for (phenylenevinylene)s,[13,14] although the importance of the dihedral angles between these segments has been pointed out before.[15]

Although the establishment of precise relationships between the chemical structure and the structural organization in solid PPV-based materials appears thus of fundamental interest, and although several unsubstituted and substituted PPV oligomers have been synthesized and electrically and optically characterized,[15−21] only very few X-ray structural character-

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(2) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477.

(3) Burn, P. L.; Holmes, A. B.; Kraft, A. B.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47.

(4) Yang, Z.; Sokolik, I.; Karasz, F. E. *Macromolecules* **1993**, *26*, 1188.

(5) Hilberer, A.; Brouwer, H.-J.; van der Scheer, B.-J.; Wildeman, J.; Hadziioannou, G. *Macromolecules* **1995**, *8*, 4525.

(6) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628.

(7) Samuel, I. D. W.; Rumbles, G.; Collison, C. J. *Phys. Rev. B* **1995**, *52*, 573.

(8) Herrema, J. K.; Wildeman, J.; van Bolhuis, F.; Hadziioannou, G. *Synth. Met.* **1993**, *60*, 239.

(9) Yassar, A.; Garnier, F.; Deloffre, F.; Horowitz, G.; Ricard, L. *Adv. Mater.* **1994**, *6*, 660.

(10) Horowitz, G.; Bachet, B.; Yassar, A.; Lang, P.; Demanze, F.; Fave, J.-L. Garnier, F. *Chem. Mater.* **1995**, *7*, 1337.

(11) Servet, B.; Ries, S.; Trotel, M.; Alnot, P.; Horowitz, G.; Garnier, F. *Adv. Mater.* **1993**, *5*, 461.

(12) Karabunarliev, S.; Baumgarten, M.; Tyutyulkov, N.; Müllen, K. *J. Phys. Chem.* **1994**, *98*, 11892.

(13) Cornil, J.; dos Santos, D. A.; Beljonne, D.; Brédas, J. L. *J. Phys. Chem.* **1995**, *99*, 5604.

(14) Fahlman, M.; Bröms, P.; dos Santos, D. A.; Moratti, S. C.; Johansson, N.; Xing, K.; Friend, R. H.; Holmes, A. B.; Brédas, J. L.; Salaneck, W. R. *J. Chem. Phys.* **1995**, *102*, 8167.

(15) Woo, H. S.; Lhost, O.; Graham, S. C.; Bradley, D. D. C.; Friend, R. H.; Quattrocchi, C.; Brédas, J. L.; Schenk, R.; Müllen, K. *Synth. Met.* **1993**, *59*, 13.

(16) Meerholz, K.; Gregorius, H.; Müllen, K.; Heinze, J. *Adv. Mater.* **1994**, *6*, 671.

(17) Adachi, C.; Tsutsui, A.; Saito, S. *Appl. Phys. Lett.* **1990**, *56*, 799.

(18) Schenk, R.; Gregorius, H.; Meerholz, K.; Heinze, J.; Müllen, K. *J. Am. Chem. Soc.* **1991**, *113*, 2634.

(19) Katz, H. E.; Bent, S. F.; Wilson, W. F.; Schilling, M. L.; Ungashe, S. B. *J. Am. Chem. Soc.* **1994**, *116*, 6631.

(20) Kretzschmann, H.; Meier, H. *J. Prakt. Chem.* **1994**, *336*, 247.

(21) Yang, Z.; Geise, H. J.; Mehbod, M.; Debrue, G.; Visser, J. W.; Sonneveld, E. J.; Van't dack, L.; Gijbels, R. *Synth. Met.* **1990**, *39*, 137.

S0897-4756(96)00130-5 CCC: $12.00

Table 1. Crystallographic and Experimental Data

Crystal Data	
formula	$C_{56}H_{60}N_2O_2$
formula wt (g mol^{-1})	793.10
crystal system	triclinic
space group	$P\bar{1}$
a (Å)	5.869(1)
b (Å)	10.270(2)
c (Å)	18.426(5)
α (deg)	100.99(2)
β (deg)	92.84(2)
γ (deg)	91.67(2)
V (Å^3)	1088.1(4)
Z	1
D_{calc} (g cm^{-3})	1.210
$F(000)$	426
μ (Mo Kα) (cm^{-1})	0.72
crystal size (mm^3)	0.04 × 0.20 × 0.38
Data Collection	
T (K)	130
θ range; min, max (deg)	1.13, 26.0
data collected	4710
no. of unique data	4269
no. of rflns obsd ($F_o \geq 4.0\sigma(F_o)$)	3055
Structure and Refinement	
no. of reflections ($F_o{}^2 > 0$)	3825
no. of parameters	391
$R(F)$	0.067
$wR(F^2)$	0.181
residual ϱ (e Å^{-3})	−0.46, 0.32
(max shift)/σ(final cycle)	<0.001

izations have been carried out to date.[21] We recently reported the first single-crystal X-ray data from an *all-trans*-PPV oligomer having five phenyl rings with two *n*-octyloxy substituents attached onto the central phenyl ring.[22] The molecules appeared to organize in a monoclinic unit cell with the conjugated backbones aligned parallel and twisted out of coplanarity around the central phenyl unit.

In this paper we report on the synthesis of a new all-trans five-ring PPV oligomer bearing two cyano substituents on the vinylene segments adjacent to the central phenyl ring. X-ray data for single crystals grown from solution are presented, and the influence of cyano substitution on aspects of conformation and packing in solid-state PPV oligomers is discussed.

Experimental Section

Measurements. NMR spectra were recorded (chloroform-*d* solutions) at 500 MHz (^{1}H), 125 MHz (^{13}C) on a Unity *plus* spectrometer operating in the Fourier transform mode. All chemical shifts reported were externally referenced to TMS (0 ppm). Elemental analyses were carried out at the Microanalytical Department of the University of Groningen. IR spectra were recorded as thin films on a KBr pellet on a Mattson Instruments FT-IR spectrometer.

Materials. Styrene, *p*-bromobenzaldehyde, palladium acetate (Pd(OAc)$_2$), tri-*o*-tolylphosphine, *tert*-butyl alcohol, and tetra-*n*-butylammonium hydroxide (0.1 N solution in 2-propanol/methanol) were obtained from Janssen Chimica, Aldrich Chemicals, or Merck and used as received. Triethylamine was dried over potassium hydroxide and THF was distilled from lithium aluminum hydride before use. 1,4-Bis(bromomethyl)-2,5-bis(*n*-octyloxy)benzene was prepared according to a literature procedure.[23] All reactions were performed under a dry argon atmosphere.

Scheme 1. Reaction Scheme for the Synthesis of 3 (R = *n*-Octyloxy)

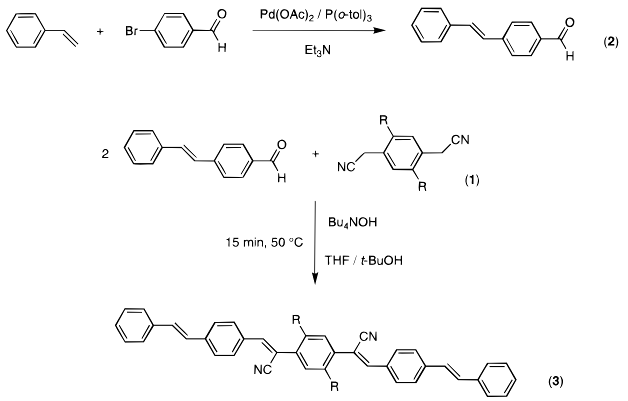

Table 2. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Displacement Parameters for Non-H Atoms with Estimated Standard Deviations in Parentheses ($U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$)

	x	y	z	U_{eq} (Å^2)
O(1)	0.5580(3)	0.68434(16)	0.13034(9)	0.0285(5)
N(1)	−0.1458(4)	0.6865(2)	−0.07285(11)	0.0283(6)
C(1)	0.6662(4)	0.4838(2)	0.05147(12)	0.0226(7)
C(2)	0.5298(4)	0.5919(2)	0.06614(12)	0.0221(7)
C(3)	0.3552(4)	0.6107(2)	0.01469(12)	0.0204(6)
C(4)	0.1920(4)	0.7192(2)	0.02612(12)	0.0203(6)
C(5)	0.2067(4)	0.8271(2)	0.08126(13)	0.0231(7)
C(6)	0.0528(4)	0.9347(2)	0.10318(12)	0.0200(6)
C(7)	0.1228(4)	1.0270(2)	0.16785(12)	0.0211(7)
C(8)	−0.0120(4)	1.1281(2)	0.19829(13)	0.0224(7)
C(9)	−0.2266(4)	1.1446(2)	0.16532(12)	0.0204(6)
C(10)	−0.2937(4)	1.0564(2)	0.09921(13)	0.0227(7)
C(11)	−0.1595(4)	0.9533(2)	0.06876(13)	0.0231(7)
C(12)	−0.3808(4)	1.2471(2)	0.19681(13)	0.0222(7)
C(13)	−0.3577(4)	1.3184(2)	0.26552(13)	0.0239(7)
C(14)	−0.5150(4)	1.4147(2)	0.30169(12)	0.0221(7)
C(15)	−0.4669(4)	1.4757(2)	0.37585(13)	0.0252(7)
C(16)	−0.6148(4)	1.5627(2)	0.41389(14)	0.0271(7)
C(17)	−0.8164(4)	1.5904(2)	0.37896(14)	0.0286(7)
C(18)	−0.8657(4)	1.5322(2)	0.30510(14)	0.0286(7)
C(19)	−0.7176(4)	1.4461(2)	0.26673(14)	0.0247(7)
C(20)	0.0017(4)	0.7020(2)	−0.02822(12)	0.0207(6)
C(21)	0.7338(4)	0.6682(2)	0.18394(13)	0.0237(7)
C(22)	0.7473(4)	0.7938(2)	0.24256(13)	0.0253(7)
C(23)	0.5342(5)	0.8207(2)	0.28576(13)	0.0264(7)
C(24)	0.5590(5)	0.9533(2)	0.33976(14)	0.0287(8)
C(25)	0.3460(4)	0.9954(2)	0.38032(14)	0.0280(8)
C(26)	0.3889(4)	1.1226(2)	0.43783(14)	0.0280(8)
C(27)	0.1798(5)	1.1754(3)	0.47708(14)	0.0314(8)
C(28)	0.0140(5)	1.2361(3)	0.42806(17)	0.0373(9)

(4-(Cyanomethyl)-2,5-bis(*n*-octyloxy)phenyl)acetonitrile (1). To a solution of 1,4-bis(bromomethyl)-2,5-bis(*n*-octyloxy)benzene (3.40 g, 6.52 mmol) in 15 mL of DMF was added NaCN (1.60 g, 32.6 mmol), and the mixture was refluxed overnight. The reaction mixture was cooled to room temperature and poured into 50 mL of NaOH (0.5 M solution in water). The solid product was filtered off, washed with methanol several times, redissolved in chloroform, washed with brine twice, and purified by repeated crystallization from ether/chloroform. Yield 3.26 g, 60%; mp 85−87 °C. ^{1}H NMR δ 0.89 (t, J = 6.6 Hz), 1.30 (m), 1.46 (qui, J = 6.2 Hz), 1.80 (qui, J = 6.6 Hz), 3.70 (s), 3.97 (t, J = 6.6 Hz), 6.91 (s) ppm. ^{13}C NMR δ 14.27, 18.83, 22.84, 26.26, 29.40, 29.45, 29.51, 31.99, 69.26, 112.91, 117.99, 119.37, 150.25 ppm. IR 2938 (s), 2918 (s), 2853 (m), 2250 (w), 1518 (m), 1473 (m), 1428 (m), 1412 (w), 1395 (m), 1312 (w), 1227 (s), 1190 (w), 1043 (m), 1005 (w), 876 (w), 865 (w), 771 (w), 759 (w), 720 (w) cm^{-1}.

4-Styrylbenzaldehyde (2). A mixture of styrene (1.04 g, 10 mmol), *p*-bromobenzaldehyde (1.85 g, 10 mmol), Pd(OAc)$_2$ (0.044 g, 0.20 mmol), tri-*o*-tolylphosphine (0.142 g, 0.46 mmol), and triethylamine (10 mL) was placed in a heavy-wall pressure tube. The tube was degassed, closed (Teflon

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[22] Gill, R. E.; Meetsma, A.; Hadziioannou, G. *Adv. Mater.* **1996**, *8*, 212.

[23] Moratti, S. C.; Cervini, R.; Holmes, A. B.; Baigent, D. R.; Friend, R. H.; Greenham, N. C.; Gruner, J.; Hamer, P. J. *Synth. Met.* **1995**, *71*, 2117.

Table 3. Selected Data on the Geometry (Standard Deviations in the Last Decimal Place Are Given in Parentheses)

	Interatomic Distances (Å)		
O(1)–C(2)	1.368(3)	C(8)–C(9)	1.400(3)
O(1)–C(21)	1.428(3)	C(9)–C(10)	1.404(3)
N(1)–C(20)	1.150(3)	C(9)–C(12)	1.462(3)
C(1)–C(2)	1.380(3)	C(10)–C(11)	1.386(3)
C(1)–C(3)a	1.404(3)	C(12)–C(13)	1.335(3)
C(2)–C(3)	1.404(3)	C(13)–C(14)	1.462(3)
C(3)–C(4)	1.482(3)	C(14)–C(15)	1.402(3)
C(4)–C(5)	1.351(3)	C(14)–C(19)	1.399(3)
C(4)–C(20)	1.446(3)	C(15)–C(16)	1.382(3)
C(5)–C(6)	1.457(3)	C(16)–C(17)	1.382(3)
C(6)–C(7)	1.409(3)	C(17)–C(18)	1.391(4)
C(6)–C(11)	1.405(3)	C(18)–C(19)	1.380(3)
C(7)–C(8)	1.374(3)		
	Bond Angles (deg)		
C(2)–O(1)–C(21)	118.90(18)	C(8)–C(9)–C(10)	117.2(2)
C(2)–C(1)–C(3)a	123.3(2)	C(8)–C(9)–C(12)	123.2(2)
O(1)–C(2)–C(1)	122.1(2)	C(10)–C(9)–C(12)	119.6(2)
O(1)–C(2)–C(3)	117.42(19)	C(9)–C(10)–C(11)	122.1(2)
C(1)–C(2)–C(3)	120.5(2)	C(6)–C(11)–C(10)	120.5(2)
C(2)–C(3)–C(4)	125.1(2)	C(9)–C(12)–C(13)	124.9(2)
C(2)–C(3)–C(1)a	116.2(2)	C(12)–C(13)–C(14)	127.2(2)
C(4)–C(3)–C(1)a	118.7(2)	C(13)–C(14)–C(15)	119.0(2)
C(3)–C(4)–C(5)	126.2(2)	C(13)–C(14)–C(19)	123.2(2)
C(3)–C(4)–C(20)	114.16(19)	C(15)–C(14)–C(19)	117.7(2)
C(5)–C(4)–C(20)	119.7(2)	C(14)–C(15)–C(16)	121.6(2)
C(4)–C(5)–C(6)	132.4(2)	C(15)–C(16)–C(17)	119.9(2)
C(5)–C(6)–C(7)	115.7(2)	C(16)–C(17)–C(18)	119.3(2)
C(5)–C(6)–C(11)	127.3(2)	C(17)–C(18)–C(19)	120.9(2)
C(7)–C(6)–C(11)	116.9(2)	C(14)–C(19)–C(18)	120.5(2)
C(6)–C(7)–C(8)	122.3(2)	N(1)–C(20)–C(4)	178.1(2)
C(7)–C(8)–C(9)	120.9(2)	O(1)–C(21)–C(22)	106.90(18)
	Torsion Angles (deg)[a]		
C(21)–O(1)–C(2)–C(1)	−0.2(3)	C(5)–C(6)–C(11)–C(10)	175.7(2)
C(21)–O(1)–C(2)–C(3)	179.9(3)	C(7)–C(6)–C(11)–C(10)	−1.7(3)
C(2)–O(1)–C(21)–C(22)	171.68(19)	C(6)–C(7)–C(8)–C(9)	−0.7(3)
C(3)a–C(1)–C(2)–O(1)	−178.3(2)	C(7)–C(8)–C(9)–C(10)	−1.9(3)
C(3)a–C(1)–C(2)–C(3)	1.6(3)	C(7)–C(8)–C(9)–C(12)	177.5(2)
C(2)–C(1)–C(3)a–C(2)a	−1.5(3)	C(8)–C(9)–C(10)–C(11)	2.7(3)
C(2)–C(1)–C(3)a–C(4)a	177.0(2)	C(12)–C(9)–C(10)–C(11)	−176.8(2)
O(1)–C(2)–C(3)–C(4)	−3.2(3)	C(8)–C(9)–C(12)–C(13)	−13.5(4)
O(1)–C(2)–C(3)–C(1)a	178.46(19)	C(10)–C(9)–C(12)–C(13)	165.9(2)
C(1)–C(2)–C(3)–C(4)	176.9(2)	C(9)–C(10)–C(11)–C(6)	−0.9(3)
C(1)–C(2)–C(3)–C(1)a	−1.4(3)	C(9)–C(12)–C(13)–C(14)	−175.1(2)
C(2)–C(3)–C(4)–C(5)	11.2(4)	C(12)–C(13)–C(14)–C(15)	177.0(2)
C(2)–C(3)–C(4)–C(20)	−168.3(2)	C(12)–C(13)–C(14)–C(19)	−0.6(4)
C(1)a–C(3)–C(4)–C(5)	−170.5(2)	C(13)–C(14)–C(15)–C(16)	−176.9(2)
C(1)a–C(3)–C(4)–C(20)	10.1(3)	C(19)–C(14)–C(15)–C(16)	0.8(3)
C(3)–C(4)–C(5)–C(6)	−174.1(2)	C(13)–C(14)–C(19)–C(18)	176.3(2)
C(20)–C(4)–C(5)–C(6)	5.4(4)	C(15)–C(14)–C(19)–C(18)	−1.3(3)
C(4)–C(5)–C(6)–C(7)	176.2(2)	C(14)–C(15)–C(16)–C(17)	0.5(3)
C(4)–C(5)–C(6)–C(11)	−1.2(4)	C(15)–C(16)–C(17)–C(18)	−1.4(3)
C(5)–C(6)–C(7)–C(8)	−175.2(2)	C(16)–C(17)–C(18)–C(19)	0.9(3)
C(11)–C(6)–C(7)–C(8)	2.5(3)	C(17)–C(18)–C(19)–C(14)	0.5(3)

[a] Label a indicates symmetry operation: $1 - x, 1 - y, -z$. The sign of the torsion angle is positive when, looking from atom 2 to atom 3, a clockwise motion of atom 1 would superimpose it on atom 4.

brushing), and heated to 80 °C in an oil bath. After 14 h the reaction mixture was cooled to room temperature and poured into methanol (50 mL). The precipitate was filtered off, washed with methanol three times, and dried in vacuum. Yield 1.93 g, 93%; mp 96 °C. ^{1}H NMR δ 7.14 (d, $J = 6.1$ Hz), 7.33 (d, $J = 7.0$ Hz), 7.40 (t, $J = 7.0$ Hz), 7.55 (d, $J = 7.0$ Hz), 7.66 (d, $J = 8.4$ Hz), 7.87 (d, $J = 8.1$ Hz), 10.00 (s) ppm. ^{13}C NMR δ 127.08 (2C), 127.55, 128.68, 129.02, 130.42, 132.41, 135.56, 136.76, 143.62, 191.72 ppm. IR 3026 (w), 2926 (w), 2822 (w), 2733 (w), 1695 (s), 1657 (w), 1601 (m), 1448 (m), 1389 (w), 1213 (m), 1168 (m), 970 (s), 870 (m), 818 (s), 758 (s), 714 (s) cm^{-1}.

2-{4-[1-Cyano-2-(4-styrylphenyl)vinyl]-2,5-bis(*n*-octyloxy)phenyl}-3-(4-styrylphenyl)acrylonitrile (3). The aldehyde **2** (383 mg, 1.84 mmol) and nitrile **1** (350 mg, 0.92 mmol) were dissolved in a mixture of *tert*-butyl alcohol (9 mL) and THF (3 mL) at 50 °C. Potassium *tert*-butoxide (10.32 mg, 0.184 mmol) and tetra-*n*-butylammonium hydroxide (0.921 mL, 0.92 mmol) were added quickly. After 15 min the reaction mixture was poured into acidified methanol. The orange precipitate was filtered off and washed with methanol three times. Pure **3** was obtained as orange plate-shaped crystals after repeated crystallization from a chloroform/*n*-hexane mixture. Yield 0.61 g, 83%; mp 153 °C. ^{1}H NMR δ 0.87 (t, $J = 7.0$ Hz, C28), 1.2–1.4 (m, C24–27), 1.50 (qui, $J = 7.7$ Hz, C23), 1.86 (qui, $J = 7.0$ Hz, C22), 4.08 (t, $J = 6.6$ Hz, C21), 7.11 (s, C1), 7.14 (d, $J = 16.1$ Hz, C13), 7.22 (d, $J = 16.5$ Hz, C12), 7.30 (t, $J = 7.3$ Hz, C17), 7.39 (t, $J = 7.7$ Hz, C16), 7.56 (d, $J = 7.3$ Hz, C15), 7.61 (d, $J = 7.8$ Hz, C8), 7.72 (s, C5), 7.91 (d, $J = 8.4$ Hz, C7) ppm. ^{13}C NMR δ 13.99, 22.55, 26.16, 29.15, 29.22, 29.26, 31.69, 69.77, 107.24, 114.43, 118.13, 125.43, 126.65, 126.77, 127.60, 128.02, 128.67, 129.72, 130.50, 133.05, 136.83, 139.53, 146.02, 150.57 ppm. IR 3027 (m), 2926 (s), 2855 (s), 2214 (w), 1599 (m), 1511 (m), 1467 (m), 1449 (m), 1424 (m), 1355 (m), 1277 (w), 1255 (s), 1181 (w), 1021 (w), 973 (m), 917 (w), 853 (w), 819 (m), 783 (w), 752 (m), 720 (w) cm^{-1}. Elemental anal. calcd: C 84.47; H 7.86; O 4.09; N 3.58. Found: 85.08; H 7.67; O 4.11; N 3.66.

X-ray Diffraction. Data collection was performed using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,073$ Å) on a Nonius CAD4F diffractometer. The intensities of three standard reflections, which were measured every 2 h, 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.[24] The structure was solved by direct methods with SHELXS86.[25] Crystal data and experimental details are given in Table 1.

Suitable orange plate-shaped crystals of compound **3** were obtained by recrystallization from a chloroform/*n*-hexane solvent mixture. A crystal of approximate dimensions of $0.04 \times 0.20 \times 0.38$ mm^3 was mounted on top of a glass fiber and transferred into the cold nitrogen stream of the low-temperature unit. Cell constants and an orientation matrix for the data collection were obtained from a least-squares refinement of 22 reflections in the range $11.46° < \theta < 23.61°$. Reflection profiles showed large anisotropic mosaicity (sheet structure); this mosaicity did not allow the use of a narrower scan angle. The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with full-matrix least-squares procedures.[26] A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms, of which the coordinates and isotropic thermal displacement parameters were refined. Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $R(F) = 0.067$ for 3055 reflections with $F > 4.0\sigma(F)$ and 391 parameters. The final difference map showed no unusual features, with no significant peak having chemical meaning above the general background.

Results and Discussion

Synthesis. The synthetic route for the dicyano-substituted PPV oligomer **3** is outlined in Scheme 1. The five-ring oligomer was formed in a Knoevenagel condensation of (4-(cyanomethyl)-2,5-bis(*n*-octyloxy)phenyl)acetonitrile (**1**) and 4-styrylbenzaldehyde (**2**) according to a procedure previously reported by Greenham et al.[6] The Knoevenagel condensation needs careful control of reaction conditions in order to avoid possible side reactions such as Michael addition of nucleophiles to the newly formed vinylene linkage or direct attack on the cyano group. The aldehyde **2** was prepared in a Heck coupling of styrene and *p*-bromobenzaldehyde under increased pressure. The Heck coupling is known to be a convenient reaction toward all-trans carbon double bonds with almost no side reactions.[27,28]

Crystal Structure. The crystal data and numerical details on data collection and refinement for **3** are given in Table 1. The unit cell was defined as triclinic, space group $P\bar{1}$, containing one discrete molecule. A short intramolecular C−H···O bond is observed: O1···H5 = 2.09 Å (the sum of the van der Waals radii is 2.72 Å). The molecule has a crystallographically imposed center of inversion. The asymmetric unit contains one-half molecule. The final fractional atomic coordinates and equivalent isotropic thermal displacement parameters are given in Table 2. Molecular geometry data are collected in Table 3. The labeling scheme of the atoms and the configuration are shown in the ORTEP drawing (Figure 1). Figure 2 presents two stereoviews of the crystal, and Figure 3a,b show two representations of the crystal packing, viewed perpendicular to and along the molecular axis, respectively. The molecule has a remarkable “wavelike” shape which involves deviations from planarity of the vinylene moieties as well as of the rings. This bending is strongest for the vinylene moieties, for which the dihedral angles are −174° (C3−C4−C5−C6) and −175° (C9−C12−C13−C14), respectively. Such distortions indicate the presence of considerable packing forces. This is corroborated by the value of the crystal density, 1.210 g cm^{-3}, which is almost 10% higher than that of the monoclinic crystalline phase of the analogous compound without cyano substituents[22] (which will be referred to as the “dioctyloxy compound”), for which $D_{\text{calc}} = 1.107$ g cm^{-3}. The introduction of the cyano groups has obviously strongly enhanced the intermolecular attraction.

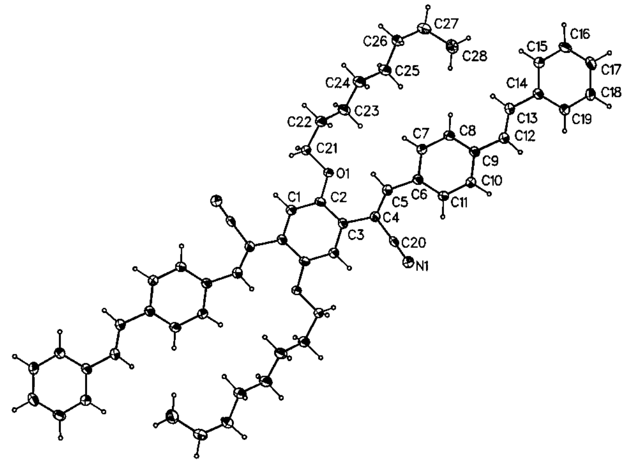

Figure 1. Perspective ORTEP drawing of the non-hydrogen atoms of **3** with the atom-labeling scheme for the non-hydrogen atoms. All non-hydrogen atoms are represented by their thermal displacement vibrational ellipsoids drawn to encompass 50% of the electron density; the hydrogen atoms are drawn with an arbitrary radius.

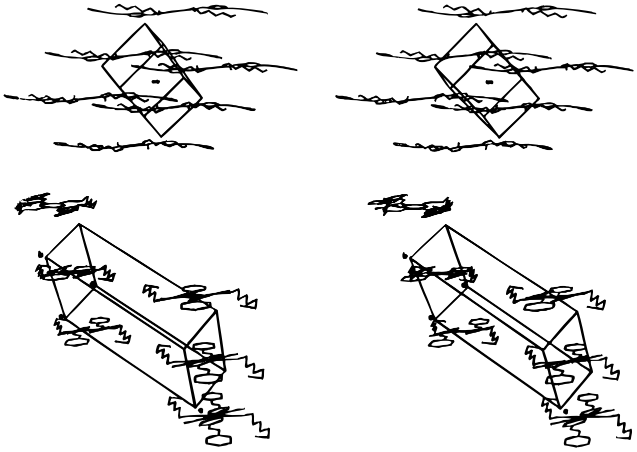

Figure 2. Two stereoviews of the crystal of **3**.

Any molecule has, roughly speaking, four of its rings exposed, in a face-to-face fashion, to four rings of a neighbor molecule related by a translation along the *b* axis. The intermolecular distance is approximately 8 Å, and the space between is occupied by the octyloxy substituents of neighboring molecules related through translations along the *a* axis. No π−π interaction is therefore expected for molecules related via the *b* axis. Neither does one expect π−π interaction for neighbors

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(24) Wilson, A. J. C., Ed., *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C.

(25) Sheldrick, G. M. *Acta Crystallogr. A* **1990**, *46*, 467.

(26) Sheldrick, G. M. SHELXL93. *Program for the refinement of Crystal Structures*; University of Göttingen, Germany, 1993.

(27) Heck, R. F. *Org. React.* **1982**, *27*, 345.

(28) Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules* **1993**, *26*, 5281.

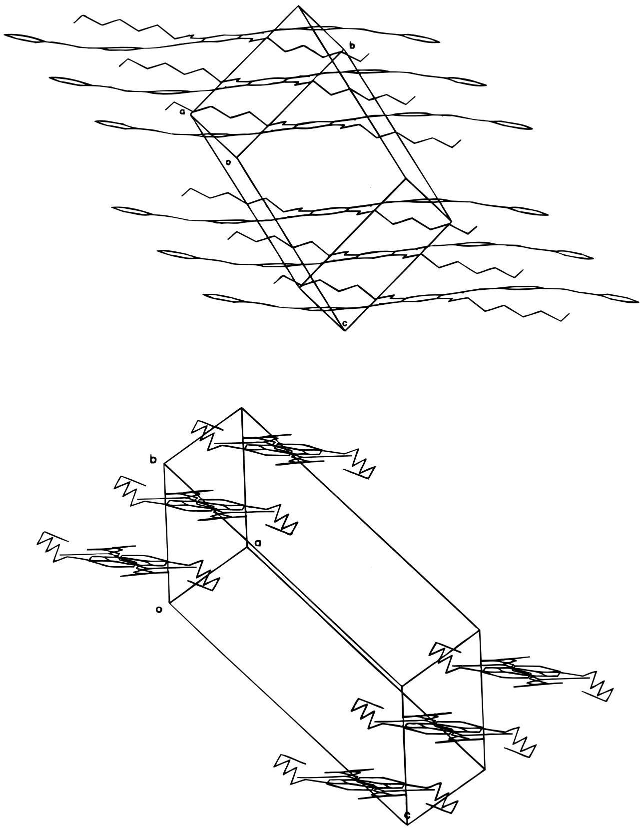

Figure 3. Packing arrangement of **3** in the unit cell, viewed perpendicular to (A) and along (B) the long molecular axis.

along the *a* axis, since the phenyl rings are found to be both laterally and axially shifted instead of above each other, in a view perpendicular to the plane of the rings (Figure 4). The axial shift, which amounts to approximately half the length of a styryl unit, is an essential aspect, since it serves to bring the nitrogen atom of the cyano group above the center of the middle phenyl ring of the neighbor molecule. This is readily attributed to a strong Coulomb attraction between the two: the cyano group bears a negative charge, while the central phenyl ring is positively charged due to its octyloxy substituents. (Our semiempirical AM1 quantum-chemical calculations, based on the conformation in the crystal, predict these charges to be −0.15 and +0.07 electron units, respectively). There is a distinct out-of-plane bending of the cyano group (a C1′−C3−C4−C20 dihedral of 10.1°), which brings the nitrogen atom at a distance of only 3.3 Å above the ring. The nitrogen atom is at the same time very close to the penultimate, almost neutral ring of a second neighbor (which is related to the former neighbor via the *b* axis) at a distance which is only about 0.1 Å larger. Although the electrostatic interactions are only operative within "ribbons" consisting of molecules related by *a*-axis translations, the cohesive forces between these ribbons are apparently quite strong and result in the close packing that imposes the wave shape on the molecules.

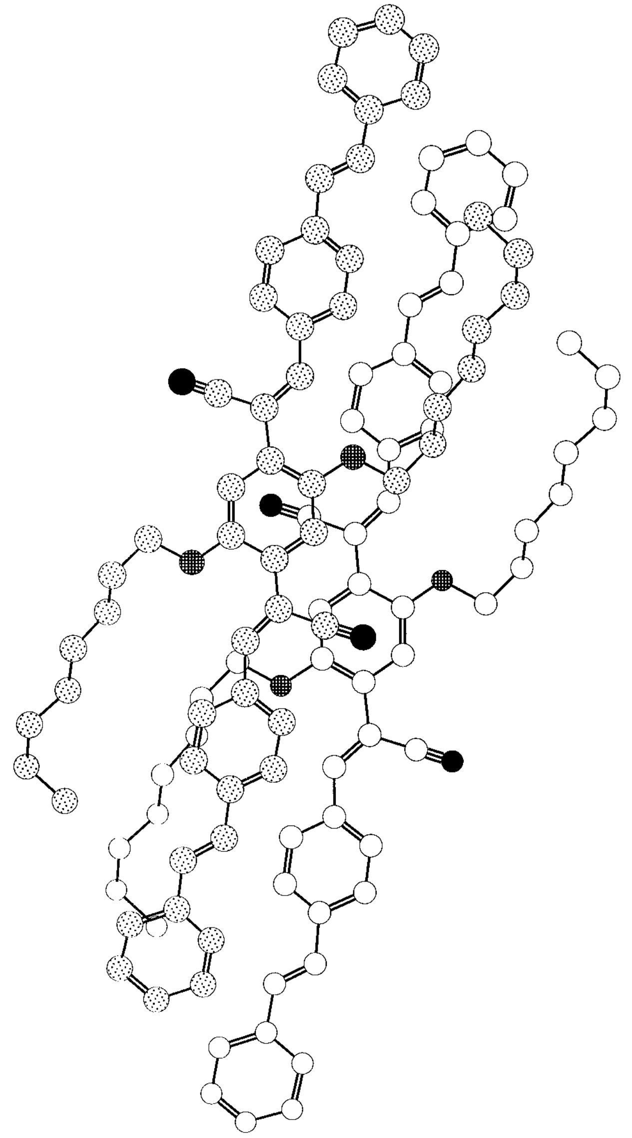

Figure 4. Top view of two molecules in the unit cell, related by a translation along the *a* axis. The cyano groups of one molecule are found above the center of the middle ring of neighbor molecules. Atom size drawn decreases with increasing distance from point of observation. Atom patterns: (none) carbon atoms of rear molecule; (speckled) carbon atoms of front molecule; (cross-hatched) oxygen; (black) nitrogen.

The octyloxy tail is stretched at the periphery of the backbone, somewhat above (below) the undulating plane. Remarkably, the penultimate ring is rotated sideways over ca. 15° to create space for the tail, especially for its terminal methyl unit which is directed inward. Since the dihedral angles across the single bonds on one side of this ring have a sign opposite to those on the other side, the overall impression of the arrangement of rings is one of moderate coplanarity. This contrasts with the dioctyloxy compound, for which all the dihedrals have the same sign, resulting in a helixlike arrangement. The behavior of the octyloxy substituents is also very distinct. Whereas in the crystal of the dioctyloxy compound, the tails form layers characterized by considerable positional disorder of the atoms, the position of the tail in the unit cell of the cyano-substituted compound is well-defined. This is probably related to our observation that crystallization proceeds much more readily for the cyano derivative than for the dioctyloxy compound.

A further difference concerns the orientation of the C4−C5 double bond. The introduction of the bulky cyano group causes an almost 180° rotation around the C3−C4 single bond. These different conformations in the crystal reflect the large change in the depth, shape and position of the minimum of the torsion potential energy associated with the dihedral C2−C3−C4−C5 upon introduction of the cyano group, as predicted for isolated molecules by our quantum-chemical calculations. In the crystal, contrary to the prediction for isolated molecules, the vinylene segment is more nearly coplanar with the central phenyl ring in the case of the cyano compound (11.2° versus −163° for the dioctyloxy analogue), which underlines the strong influence of the intermolecular interactions on the molecular geometry.

We suggest that the packing mechanism presented above for our model compound, driven by Coulomb interactions, may very well be operative in the solid state of cyano-substituted polymers as well.[7]

Supporting Information Available: Tables of hydrogen atom positions, thermal displacement parameters, comprehensive lists of bond distances and angles and tables of (F_o), (F_c), and $\sigma(F)$ (5 pages); observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Acknowledgment. Jan K. Herrema is gratefully acknowledged for his help in the NMR analysis. This work was financially supported by Stichting Scheikundig Onderzoek Nederland (SON) and Stichting Toegepaste Wetenschappen (STW).

CM9601300