Bull. Chem. Soc. Jpn., ***68***, *1281—1288(1995)*

Crystal Structures of Two Isomeric Series of Mesogens, 4-Cyanophenyl 4-*n*-Alkoxybenzoates and 4-*n*-Alkoxyphenyl 4-Cyanobenzoates

Hitoe Iki and Kayako Hori*

Department of Chemistry, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112

(Received August 18, 1994)

Single crystal X-ray analysis has been done for two isomeric series, 4-cyanophenyl 4-*n*-alkoxybenzoates (CP*n*OB, n=6, 7, and 8) with a phase sequence of crystal–nematic–isotropic and 4-*n*-alkoxyphenyl 4-cyanobenzoates (*n*OPCB, n=6, 7, and 8), which have the smectic A phase as well as the nematic phase for n=7 and 8. In the crystals of CP6OB and CP8OB, close arrangements between CN groups of a pair of molecules are observed, though in the latter crystal two carbonyloxy groups between another pair of molecules are also closely arranged. For CP7OB and 6OPCB, CN and carbonyloxy groups come close to each other between a pair of molecules. These pairs of molecules have half-and-half overlappings (imbricate structures), being closely related to the nematic structure. On the other hand, the crystal of 7OPCB has a distinct smectic-like layer structure with infinite networks of close arrangement of the CN groups, while in the crystal of 8OPCB dimers formed by association of the CN and carbonyloxy groups are arranged in an alternate stacking of core moieties and chains, also closely related to a smectic-like layer structure. The different features of the two series are discussed in terms of the different magnitudes of the overall dipole moments along the molecular long axes caused by opposite directions of the carbonyloxy groups between the two series.

We have found good correlations between crystal structures and mesophase behavior by systematic single crystal structure analysis for several series of chiral biphenyl esters with different mesophase sequences according to slightly different molecular configurations.[1)] On the other hand, a complicated crystalline polymorphism was found for mesogenic 4-cyano-4′-heptyloxybiphenyl (7OCB),[2,3)] which has a fairly simple molecular structure.

Two isomeric series, 4-cyanophenyl 4-*n*-alkoxybenzoates (CP*n*OB) and 4-*n*-alkoxyphenyl 4-cyanobenzoates (*n*OPCB), have different mesophase sequences.[4)] The former series has a phase sequence of crystal–nematic–isotropic,[5)] while the members of the latter series have phase sequences, crystal–nematic–isotropic for $n=6$, crystal–Sm A–nematic–isotropic for $n=7$ and 8 and crystal–Sm A–isotropic for $n=9$, 10, and 12. X-Ray measurements for the mesophases of *n*OPCB and CP10OB showed that these mesophases are composed of dimers of molecules.[6)] It was also shown that the length of a dimer of CP10OB is shorter than that of 10OPCB. For CP5OB, it was reported[7)] that the crystal has a non-parallel arrangement of molecular long axes, being responsible for the fact that the compound is only a monotropic nematogen. To identify the intermolecular interactions controlling these different mesophase sequences, we have analyzed the crystal structures for n=6, 7, and 8 of both series.

Experimental

Compounds. All the compounds were synthesized from commercially available benzoic acids (or 4-cyanobenzoyl chloride) and phenols (Tokyo Kasei Industry Co, Ltd.) by conventional methods.

X-Ray Crystal Structure Analysis. Cell parameter measurements and reflection data collection were done on an AFC-7R four-circle diffractometer using Cu $K\alpha$ radiation monochromated by graphite (λ=1.54184 Å) at room temperature. 2θ–ω mode with the scan rate of 8° min^{-1} (ω) was used up to 2θ=120°. Three standard reflections were measured after every 150 reflections. No significant variation was observed. All the data were corrected for Lorentz and polarization factors. Absorption corrections by ψ scan method were applied for CP7OB and 7OPCB. Detailed experimental conditions, crystal data, and final results of refinements are summarized in Table 1. Two crystal forms were obtained for 6OPCB; i.e., plate and needle crystals. The needle crystal obtained from an acetone solution with a small amount of water collapsed too rapidly to obtain diffraction data at room temperature.

All the structures were solved by applying the teXsan program package.[8)] The structures of CP6OB, CP8OB, 7OPCB, and 8OPCB were refined by full-matrix least-squares on F using the same package, while those of CP7OB and 6OPCB were refined by full-matrix least-squares on F^2 with restrained conditions for a few bonds by using SHELXL93.[9)] All the non-hydrogen atoms were refined

Table 1. Experimental Details, Crystal Data and Final Results of Refinements

	CP6OB	CP7OB	CP8OB	6OPCB	7OPCB	8OPCB
Solvents for crystal growth	Acetone–water	Diethyl ether–methanol	Acetone–water	Diethyl ether–methanol	Ethyl acetate–1-butanol	Acetone–methanol
Growth temp	R.T.	5 °C	5 °C	17 °C	17 °C	17 °C
Cryst. habit	Plate	Plate	Needle	Plate	Plate	Needle
Cryst. size/mm	0.1×0.3×0.5	0.3×0.3×0.5	0.1×0.2×0.5	0.1×0.5×0.7	0.1×0.3×0.5	0.3×0.3×0.5
l.s. for cell const.[a)]	25 (55—57)	22 (56—58)	25 (55—57)	25 (56—57)	23 (41—54)	25 (56—57)
Space group	$P\bar{1}$	$P2_1/a$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	10.506(2)	46.163(6)	11.164(3)	9.338(2)	39.184(5)	21.870(2)
b/Å	10.906(2)	9.607(5)	13.434(2)	11.247(3)	7.016(9)	14.549(4)
c/Å	8.484(2)	8.474(5)	6.719(2)	9.071(2)	6.833(6)	6.195(4)
α/°	96.34(2)	90	100.20(2)	94.27(2)	90	90
β/°	113.65(1)	94.85(3)	94.01(2)	99.08(2)	92.23(4)	94.33(2)
γ/°	90.17(2)	90	85.50(2)	107.71(2)	90	90
V/Å^3	883.8(3)	3744(2)	987.2(4)	888.6(4)	1877(2)	1965(1)
Z	2	8	2	2	4	4
d_x/g cm^{-3}	1.22	1.20	1.18	1.21	1.19	1.19
μ/cm^{-1}	6.57	6.39	5.90	6.52	6.38	6.28
F(0 0 0)	344	1440	376	344	720	752
R_1[b)]	0.051	0.067	0.050	0.077	0.110	0.081
R_w[c)] or [R_{w2}[d)]]	0.032	[0.172]	0.038	[0.205]	0.095	0.094
No. of unique refl.	2632	5580	2929	2652	2580	3340
No. of obsd refl.	1318 (>3$\sigma(I)$)	4621 (>4$\sigma(F_o)$)	1571 (>3$\sigma(I)$)	2177 (>4$\sigma(F_o)$)	1672 (>3$\sigma(I)$)	2882 (>3$\sigma(I)$)
Max. shift/error	0.17	0.28	0.10	0.47	0.38	0.05
$\Delta\rho$/e A^{-3}	0.13	0.26	0.13	0.34	0.31	0.38

a) Number of reflections for least-squares fit with 2θ range (°) in a parenthesis. b) $R_1=\sum||F_o|-|F_c||/\sum|F_o|$ for obsd reflections. c) $R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{0.5}$ for obsd reflections, where $w=1/\sigma^2(F_o)$. d) $R_{w2}=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$ for all reflections, where w was determined by the program SHELXL93.

anisotropically. Hydrogen atoms found in the difference Fourier maps and calculated geometrically were refined isotropically. Scattering factors were taken from the International Tables for Crystallography.[10)]

In spite of the restraint conditions mentioned above, bond lengths of the twisted moiety of the paraffin chain of 6OPCB, C(16)–C(17) and C(18)–C(19) (1.483(6) and 1.437(6) Å, respectively) appeared significantly shorter than the ideal value. This may be due to a thermal puckering motion of the twisted chain, because C(17) and C(18) had slightly larger temperature factors than adjacent atoms. However, it was impossible to divide these atoms into precise disordered structures, because no significant peaks were found around the atoms. The large R value for 7OPCB is due to the poor crystallinity in spite of repeated attempts at crystallization. Final atomic coordinates are shown in Tables 2, 3, 4, 5, 6, and 7.[11)]

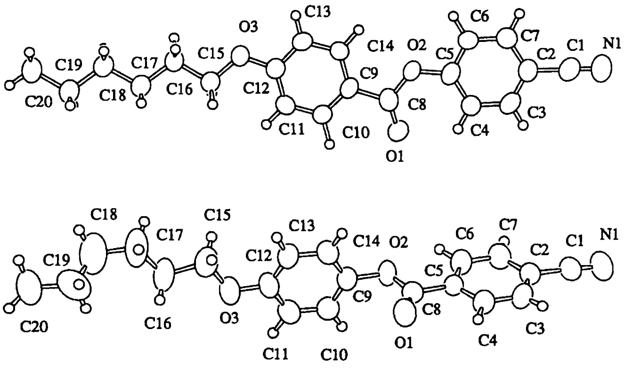

Fig. 1. ORTEP drawings[12)] of CP6OB (upper) and 6OPCB (lower) with 50% probability thermal ellipsoids.

Results and Discussion

Molecular Structures. Figure 1 shows molecular structures of CP6OB (upper) and 6OPCB (lower) with numbering schemes. The other homologues are numbered in the same schemes. There are two crystallographically independent molecules, A and B, in CP7OB, which are denoted as CP7OB-A and CP7OB-B. Two benzene rings in CP6OB are coplanar (1.0(6)°), while those in the other crystals have twisted conformations, the dihedral angles of which are 36.2(1) (CP7OB-A) and 65.3(1) (CP7OB-B), 49.2(2) (CP8OB), 88.1(1) (6OPCB), 63.1(2) (7OPCB), and 60.3(2)° (8OPCB). A carbonyloxy plane is approximately coplanar with the benzene ring, to which the C atom of the carbonyloxy group is attached, in all the molecules, with dihedral angles of 0.9(6) (CP6OB), 11.0(4) (CP7OB-A) and 1.2(3) (CP7OB-B), 8.2(6) (CP8OB), 1.8(6) (6OPCB), 7.5(6) (7OPCB), and 5.8(6)° (8OPCB). Only CP6OB has a similar molecular structure to that of CP5OB, which was reported to have an exact C_s symmetry.[7)] Paraffin chains have all-trans conformations except for 6OPCB,

Table 2. Atomic Coordinates with Their Estimated Standard Deviations in Parentheses and Equivalent Isotropic Displacement Parameters for CP6OB

Atom	x	y	z	B_{eq} [a] / Å^2
O(1)	0.2840(4)	0.4296(4)	0.0979(6)	7.8(1)
O(2)	0.3872(3)	0.5948(3)	0.2947(5)	6.0(1)
O(3)	0.9275(3)	0.3560(3)	0.2968(5)	6.1(1)
N(1)	−0.1502(5)	0.9094(5)	0.3359(7)	8.4(2)
C(1)	−0.0613(5)	0.8524(6)	0.3312(8)	6.1(2)
C(2)	0.0534(5)	0.7818(6)	0.3222(8)	5.0(2)
C(3)	0.0257(6)	0.6746(6)	0.2152(9)	6.9(2)
C(4)	0.1329(6)	0.6066(6)	0.1990(9)	7.6(2)
C(5)	0.2681(5)	0.6503(5)	0.2963(8)	5.5(2)
C(6)	0.2973(6)	0.7566(5)	0.4091(8)	5.5(2)
C(7)	0.1899(5)	0.8234(6)	0.4245(8)	6.1(2)
C(8)	0.3862(6)	0.4890(5)	0.1946(8)	5.2(2)
C(9)	0.5301(5)	0.4557(5)	0.2211(7)	4.7(2)
C(10)	0.5456(5)	0.3499(5)	0.1286(8)	5.1(2)
C(11)	0.6775(5)	0.3136(5)	0.1493(8)	5.1(2)
C(12)	0.7938(5)	0.3832(5)	0.2652(8)	4.9(2)
C(13)	0.7789(5)	0.4919(5)	0.3563(8)	6.0(2)
C(14)	0.6476(5)	0.5281(5)	0.3372(8)	5.3(2)
C(15)	0.9511(6)	0.2420(6)	0.2116(10)	5.6(2)
C(16)	1.1074(6)	0.2345(7)	0.2713(10)	5.6(2)
C(17)	1.1435(6)	0.1220(7)	0.181(1)	5.8(2)
C(18)	1.2986(6)	0.1074(8)	0.241(1)	5.7(2)
C(19)	1.3364(6)	−0.0019(7)	0.144(1)	6.0(2)
C(20)	1.4919(7)	−0.0209(10)	0.215(1)	7.2(3)

a) $B_{eq}=(8\pi^2/3)\sum\sum U_{ij}\,a_i^*\,a_j^*\,\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 3. Atomic Coordinates with Their Estimated Standard Deviations in Parentheses and Equivalent Isotropic Displacement Parameters for CP7OB

Atom	x	y	z	U_{eq} [a] / Å^2
O(1A)	0.6307(1)	0.3506(2)	0.3455(3)	0.086(1)
O(2A)	0.6512(1)	0.1401(2)	0.3865(2)	0.065(1)
O(3A)	0.5328(1)	0.0216(2)	0.6718(2)	0.070(1)
N(1A)	0.7753(1)	0.2981(3)	0.0662(3)	0.088(1)
C(1A)	0.7539(1)	0.2695(3)	0.1167(3)	0.069(1)
C(2A)	0.7270(1)	0.2364(3)	0.1857(3)	0.057(1)
C(3A)	0.7164(1)	0.3298(3)	0.2912(3)	0.061(1)
C(4A)	0.6909(1)	0.3003(3)	0.3580(3)	0.060(1)
C(5A)	0.6764(1)	0.1805(3)	0.3170(3)	0.054(1)
C(6A)	0.6868(1)	0.0859(3)	0.2143(3)	0.062(1)
C(7A)	0.7125(1)	0.1149(3)	0.1479(3)	0.065(1)
C(8A)	0.6296(1)	0.2362(3)	0.3980(3)	0.060(1)
C(9A)	0.6050(1)	0.1780(3)	0.4766(3)	0.057(1)
C(10A)	0.5833(1)	0.2691(3)	0.5133(3)	0.065(1)
C(11A)	0.5591(1)	0.2207(3)	0.5815(3)	0.065(1)
C(12A)	0.5562(1)	0.0811(3)	0.6104(3)	0.059(1)
C(13A)	0.5779(1)	−0.0116(3)	0.5745(3)	0.066(1)
C(14A)	0.6022(1)	0.0384(3)	0.5089(3)	0.063(1)
C(15A)	0.5098(1)	0.1110(3)	0.7122(4)	0.067(1)
C(16A)	0.4863(1)	0.0231(3)	0.7728(4)	0.064(1)
C(17A)	0.4620(1)	0.1103(3)	0.8291(4)	0.069(1)
C(18A)	0.4378(1)	0.0268(3)	0.8919(4)	0.067(1)
C(19A)	0.4137(1)	0.1147(3)	0.9483(4)	0.077(1)
C(20A)	0.3886(1)	0.0347(4)	1.0037(4)	0.079(1)
C(21A)	0.3658(1)	0.1253(4)	1.0695(4)	0.096(1)
O(1B)	0.7427(1)	0.1056(2)	0.6581(3)	0.086(1)
O(2B)	0.7613(1)	0.3204(2)	0.6678(2)	0.062(1)
O(3B)	0.6411(1)	0.4673(2)	0.9121(3)	0.072(1)
N(1B)	0.8945(1)	0.1430(4)	0.4759(5)	0.130(1)
C(1B)	0.8717(1)	0.1670(4)	0.5082(5)	0.090(1)
C(2B)	0.8427(1)	0.2022(3)	0.5488(4)	0.066(1)
C(3B)	0.8327(1)	0.1509(3)	0.6868(3)	0.067(1)
C(4B)	0.8053(1)	0.1880(3)	0.7271(3)	0.064(1)
C(5B)	0.7884(1)	0.2718(3)	0.6265(3)	0.054(1)
C(6B)	0.7978(1)	0.3239(3)	0.4892(4)	0.066(1)
C(7B)	0.8253(1)	0.2867(3)	0.4503(4)	0.074(1)
C(8B)	0.7400(1)	0.2255(3)	0.6862(3)	0.057(1)
C(9B)	0.7140(1)	0.2918(3)	0.7427(3)	0.052(1)
C(10B)	0.6902(1)	0.2079(3)	0.7640(3)	0.061(1)
C(11B)	0.6652(1)	0.2634(3)	0.8177(3)	0.062(1)
C(12B)	0.6641(1)	0.4026(3)	0.8533(3)	0.057(1)
C(13B)	0.6876(1)	0.4881(3)	0.8299(4)	0.067(1)
C(14B)	0.7123(1)	0.4320(3)	0.7750(3)	0.062(1)
C(15B)	0.6165(1)	0.3838(3)	0.9424(4)	0.066(1)
C(16B)	0.5946(1)	0.4743(3)	1.0140(4)	0.067(1)
C(17B)	0.5685(1)	0.3905(3)	1.0561(4)	0.068(1)
C(18B)	0.5466(1)	0.4714(3)	1.1415(3)	0.064(1)
C(19B)	0.5209(1)	0.3845(3)	1.1816(3)	0.066(1)
C(20B)	0.4983(1)	0.4611(3)	1.2662(4)	0.076(1)
C(21B)	0.4729(1)	0.3718(4)	1.3054(4)	0.092(1)

a) U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

which has a twisted paraffin chain with a torsion angle of 72.9(8)° for C(16)–C(17)–C(18)–C(19). All the bond lengths and angles are normal within experimental errors except the two bonds mentioned in the Experimental section.

Crystal Packings. Figure 2 shows the crystal structure of CP6OB viewed along a slightly skewed direction from the c axis. Atoms of the front molecules are denoted by solid circles, while those of the behind ones are shown by open circles. Molecules are piled up almost completely along the c axis with the shortest distance of 3.604(9) Å for C(7) $(x, y, z)\cdots$C(12) $(-x+1, -y+1, -z+1)$. The CN groups are also closely arranged between the molecules located at (x, y, z) and $(-x, -y+2, -z+1)$. The C···N distance, 3.601(7) Å, is slightly longer than that expected for van der Waals contact (3.25 Å)[13] but is comparable with the values observed for the 6OCB crystal (3.40 and 3.56 Å)[2] and the 7OCB needle one (3.39 and 3.55 Å).[2] In these crystals, two crystallographically independent molecules are arranged in almost the same manner with the close distances between the CN groups, as mentioned above, while the packing modes are totally different. Therefore, it is interpreted that a composing unit of these two crystals is a "dimer" formed by the close arrangement between the CN groups. Taking the large dipole moment of a CN group (4.0 D)[13] into account, it is reasonable that a strong and specific interaction is assumed between the CN groups also in the CP6OB crystal. Thus, it is considered that the crystal is composed of dimer molecules formed by the CN–CN interaction

Table 4. Atomic Coordinates with Their Estimated Standard Deviations in Parentheses and Equivalent Isotropic Displacement Parameters for CP8OB

Atom	x	y	z	B_{eq} $^{a)}/Å^2$
O(1)	0.1138(4)	0.4272(3)	0.5925(6)	6.6(1)
O(2)	−0.0291(3)	0.3156(3)	0.4922(5)	4.3(1)
O(3)	0.2894(3)	0.1778(3)	−0.2460(5)	5.0(1)
N(1)	−0.4173(5)	0.4704(4)	1.2206(7)	7.5(2)
C(1)	−0.3510(5)	0.4477(4)	1.0999(8)	4.7(2)
C(2)	−0.2648(5)	0.4164(4)	0.9435(8)	3.8(1)
C(3)	−0.1425(5)	0.4101(4)	0.9977(8)	4.1(2)
C(4)	−0.0599(5)	0.3787(4)	0.8501(8)	3.9(2)
C(5)	−0.1035(5)	0.3550(4)	0.6518(8)	3.7(1)
C(6)	−0.2248(5)	0.3631(4)	0.5944(8)	4.0(1)
C(7)	−0.3058(5)	0.3938(4)	0.7420(8)	4.4(2)
C(8)	0.0777(5)	0.3587(5)	0.4768(8)	4.1(2)
C(9)	0.1349(4)	0.3067(4)	0.2890(7)	3.3(1)
C(10)	0.2343(5)	0.3484(4)	0.2339(8)	4.2(2)
C(11)	0.2903(5)	0.3083(4)	0.0574(8)	4.1(2)
C(12)	0.2446(5)	0.2243(4)	−0.0669(8)	3.8(1)
C(13)	0.1457(5)	0.1799(4)	−0.0112(8)	4.3(2)
C(14)	0.0915(5)	0.2218(4)	0.1643(8)	3.9(2)
C(15)	0.3879(6)	0.2218(5)	−0.3190(9)	4.3(2)
C(16)	0.4184(5)	0.1540(5)	−0.5170(9)	4.0(2)
C(17)	0.5270(6)	0.1879(5)	−0.6067(9)	4.2(2)
C(18)	0.5600(6)	0.1180(5)	−0.803(1)	4.2(2)
C(19)	0.6715(7)	0.1484(6)	−0.891(1)	5.0(2)
C(20)	0.7034(6)	0.0804(5)	−1.089(1)	4.5(2)
C(21)	0.8182(7)	0.1062(6)	−1.169(1)	6.4(2)
C(22)	0.8452(8)	0.0435(7)	−1.375(1)	7.8(3)

a) $B_{eq}=(8\pi^2/3)\sum\sum U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

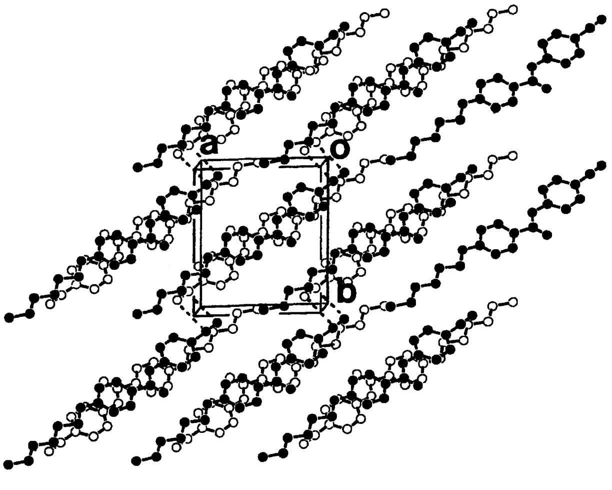

Fig. 2. Crystal structure of CP6OB viewed along a slightly skewed direction from the c axis. Atoms of front molecules are shown by solid circles and those of behind ones are shown by open circles. Close contacts between CN groups are shown by broken lines.

and half of each dimer is overlapped with half of a neighboring dimer and the other half with half of another neighbor. This feature of a half-and-half overlapping or imbricate structure, which is also observed in the 6OCB crystal,[2)] is closely related to a nematic structure.

Table 5. Atomic Coordinates with Their Estimated Standard Deviations in Parentheses and Equivalent Isotropic Displacement Parameters for 6OPCB

Atom	x	y	z	U_{eq} $^{a)}/Å^2$
O(1)	0.6206(3)	0.5905(3)	0.7420(3)	0.079(1)
O(2)	0.8070(3)	0.5726(2)	0.9181(3)	0.072(1)
O(3)	0.7494(3)	0.8973(3)	1.3731(3)	0.089(1)
N(1)	0.9707(5)	0.1987(4)	0.2904(4)	0.100(1)
C(1)	0.9254(5)	0.2524(3)	0.3729(4)	0.075(1)
C(2)	0.8709(4)	0.3238(3)	0.4775(4)	0.062(1)
C(3)	0.7457(5)	0.3630(4)	0.4290(4)	0.074(1)
C(4)	0.7002(4)	0.4351(4)	0.5280(4)	0.067(1)
C(5)	0.7764(3)	0.4700(3)	0.6755(3)	0.055(1)
C(6)	0.9007(4)	0.4294(4)	0.7237(4)	0.069(1)
C(7)	0.9461(5)	0.3563(4)	0.6246(4)	0.072(1)
C(8)	0.7247(4)	0.5507(3)	0.7785(4)	0.059(1)
C(9)	0.7782(4)	0.6535(3)	1.0279(4)	0.062(1)
C(10)	0.8533(4)	0.7813(3)	1.0411(4)	0.071(1)
C(11)	0.8396(5)	0.8592(4)	1.1569(4)	0.075(1)
C(12)	0.7516(4)	0.8107(3)	1.2607(4)	0.068(1)
C(13)	0.6738(4)	0.6829(4)	1.2450(4)	0.071(1)
C(14)	0.6874(4)	0.6037(4)	1.1270(4)	0.068(1)
C(15)	0.6814(5)	0.8556(4)	1.4942(5)	0.093(1)
C(16)	0.7127(6)	0.9705(5)	1.6097(5)	0.107(2)
C(17)	0.6410(8)	0.9370(6)	1.7421(6)	0.135(2)
C(18)	0.6882(8)	1.0401(6)	1.8747(7)	0.139(2)
C(19)	0.6253(8)	1.1406(6)	1.8522(7)	0.131(2)
C(20)	0.6508(8)	1.2346(7)	1.9911(8)	0.124(2)

a) U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Figure 3 shows the crystal structure of CP7OB viewed along a slightly skewed direction from the b axis. Atoms of the front molecules are denoted by solid circles, while those in the behind ones are shown by open circles. There are two crystallographically independent molecules, A and B. The CN and carbonyloxy groups are closely arranged between two antiparallel molecules, A (x, y, z) and B ($-x+1.5$, $y+0.5$, $-z+1$), which are stacked along the b axis; N(B)···O(1A): 3.432(6) and C(1B)···O(1A): 3.288(6) Å. On the other hand, the CN group of the molecule A(x, y, z) is also close to the carbonyloxy group of the molecule B(x, y, $z-1$), (N(A)···O(2B); 3.388(5) Å).

Figure 4 shows the crystal structure of CP8OB viewed along the c axis. Here again, CN groups have a close arrangement (C···N; 3.486(6) Å) between a pair of molecules. In addition, carbonyloxy groups of another pair of molecules are also closely arranged (O(1)···O(1), 3.387 Å). Comparing the magnitude of the dipole moments,[13)] 4.0 D for CN and 1.8 D for –COO–, however, the contribution of CN–CN interaction is expected to be dominant in the crystal. Taking two molecules related by the CN–CN interaction as a dimer unit, the crystal has also a half-and-half overlapping of the dimers.

Figure 5 shows the crystal structure of 6OPCB. The distances of the CN and carbonyloxy groups between

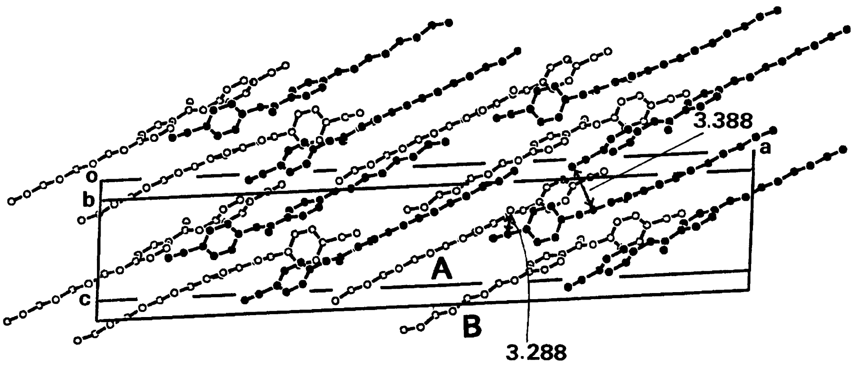

Fig. 3. Crystal structure of CP7OB. Atoms of front molecules are shown by solid circles and those of behind ones are shown by open circles. Close contacts between CN and carbonyloxy groups are shown by arrows with the distances (Å).

Table 6. Atomic Coordinates with Their Estimated Standard Deviations in Parentheses and Equivalent Isotropic Displacement Parameters for 7OPCB

Atom	x	y	z	$B_{eq}{}^{a)}/\text{Å}^2$
O(1)	0.1717(2)	0.810(1)	0.094(1)	5.0(2)
O(2)	0.1755(2)	0.4939(9)	0.050(1)	4.4(2)
O(3)	0.3083(2)	0.518(1)	0.349(1)	4.7(2)
N(1)	−0.0097(2)	0.620(1)	−0.248(1)	6.6(3)
C(1)	0.0176(3)	0.617(2)	−0.197(2)	5.3(3)
C(2)	0.0546(2)	0.625(2)	−0.133(1)	4.0(3)
C(3)	0.0693(3)	0.799(1)	−0.105(1)	4.3(3)
C(4)	0.1042(2)	0.811(2)	−0.047(1)	3.7(3)
C(5)	0.1221(2)	0.641(1)	−0.025(1)	3.5(2)
C(6)	0.1067(3)	0.467(2)	−0.053(2)	4.6(3)
C(7)	0.0727(3)	0.454(2)	−0.111(2)	5.0(3)
C(8)	0.1595(2)	0.669(2)	0.047(1)	3.8(3)
C(9)	0.2100(3)	0.494(1)	0.126(2)	3.8(3)
C(10)	0.2346(3)	0.576(1)	0.018(1)	4.3(3)
C(11)	0.2680(3)	0.581(1)	0.100(2)	4.0(3)
C(12)	0.2750(3)	0.503(1)	0.278(1)	4.0(3)
C(13)	0.2501(3)	0.413(1)	0.384(2)	4.5(3)
C(14)	0.2160(3)	0.413(1)	0.305(2)	4.4(3)
C(15)	0.3169(2)	0.459(1)	0.543(1)	4.8(3)
C(16)	0.3525(3)	0.533(2)	0.598(2)	4.8(3)
C(17)	0.3648(3)	0.462(2)	0.800(2)	4.8(3)
C(18)	0.4011(3)	0.538(2)	0.851(2)	4.6(3)
C(19)	0.4150(3)	0.464(2)	1.049(2)	5.0(3)
C(20)	0.4513(3)	0.536(2)	1.096(2)	6.3(3)
C(21)	0.4661(3)	0.458(2)	1.288(2)	8.4(4)

a) $B_{eq}=(8\pi^2/3)\sum\sum U_{ij}a_i^*a_j^*a_i\cdot a_j$.

two adjacent molecules related by an inversion center are 3.520(4) and 3.637(4) Å for N–C(8) and N–O(2), respectively. The proximity of CN and carbonyloxy groups at two points leads to a parallel arrangement of the benzene ring between the two groups, with the shortest distance of 3.691(6) Å for C(3)···C(7). Thus, it is regarded that the two molecules form a dimer and the dimers are arranged in an imbricate structure, as shown in Fig. 5.

Figure 6 shows the crystal structure of 7OPCB, in which molecules are arranged in a smectic-like layer structure. The layer plane is regarded as parallel to the *bc* plane. The tilt angle of the core moiety is about 15°. Figure 7 shows close contacts of CN groups. Short distances of N···C, 3.49(1), 3.52(2), and 3.56(2) Å are found between antiparallel CN groups, forming not a dimer but a two-dimensional network of CN–CN close contacts. The shortest distance between parallel CN groups is shown by an arrow; C···N: 3.77(2), C···C:

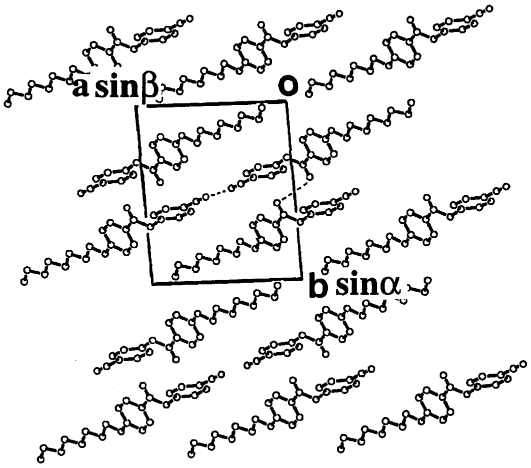

Fig. 4. Crystal structure of CP8OB viewed along the *c* axis. Close contacts between CN groups and between carbonyloxy groups are shown by broken lines.

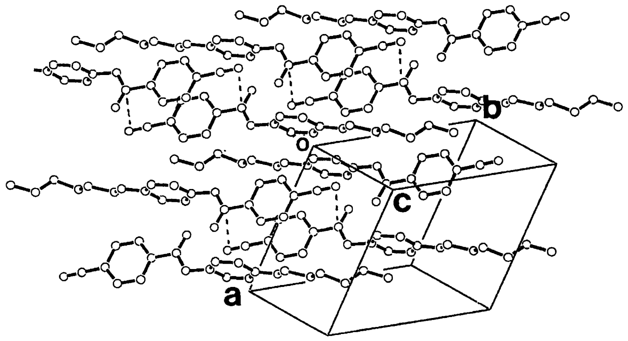

Fig. 5. Crystal structure of 6OPCB. Close contacts between CN and carbonyloxy groups are shown by broken lines.

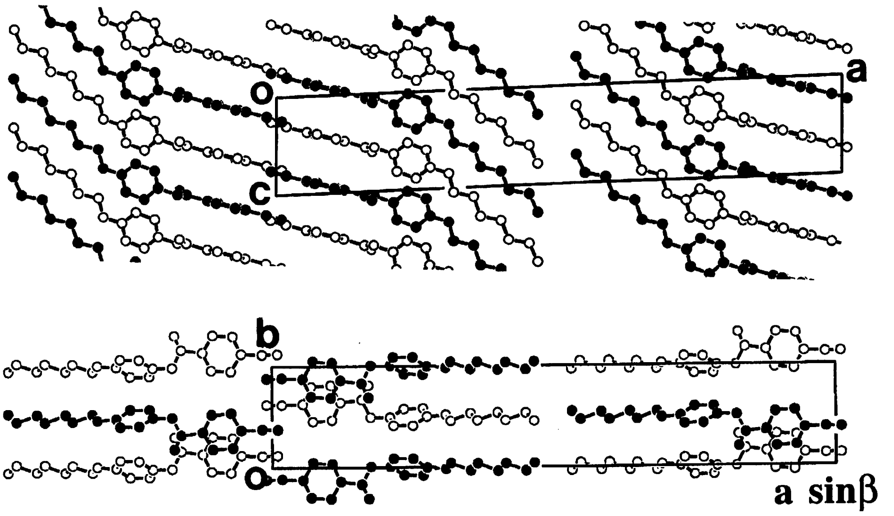

Fig. 6. Crystal structure of 7OPCB viewed along the *b* (upper) and *c* (lower) axes. Molecules in front are shown by solid circles and those in behind are shown by open circles in each figure.

Table 7. Atomic Coordinates with Their Estimated Standard Deviations in Parentheses and Equivalent Isotropic Displacement Parameters for 8OPCB

Atom	x	y	z	B_{eq}a) $/\text{Å}^2$
O(1)	0.1475(1)	0.6807(2)	0.1353(5)	6.35(8)
O(2)	0.1975(1)	0.6032(2)	0.4100(4)	5.12(7)
O(3)	0.4280(1)	0.6417(2)	0.1162(4)	4.74(7)
N(1)	−0.1071(2)	0.5864(3)	0.8669(7)	8.5(1)
C(1)	−0.0663(2)	0.5976(3)	0.7685(7)	6.0(1)
C(2)	−0.0122(2)	0.6100(3)	0.6494(7)	4.9(1)
C(3)	−0.0167(2)	0.6486(3)	0.4441(7)	5.1(1)
C(4)	0.0360(2)	0.6588(3)	0.3367(7)	4.9(1)
C(5)	0.0923(2)	0.6299(2)	0.4304(6)	4.2(1)
C(6)	0.0959(2)	0.5920(3)	0.6342(7)	5.1(1)
C(7)	0.0440(2)	0.5815(3)	0.7444(7)	5.3(1)
C(8)	0.1475(2)	0.6424(3)	0.3047(7)	4.7(1)
C(9)	0.2545(2)	0.6134(3)	0.3202(6)	4.5(1)
C(10)	0.2667(2)	0.5693(3)	0.1353(7)	5.1(1)
C(11)	0.3253(2)	0.5765(3)	0.0606(7)	4.9(1)
C(12)	0.3695(2)	0.5282(2)	0.1756(6)	4.13(9)
C(13)	0.3564(2)	0.6716(3)	0.3646(6)	4.4(1)
C(14)	0.2981(2)	0.6642(3)	0.4372(7)	4.6(1)
C(15)	0.4444(2)	0.6058(3)	−0.0866(7)	4.6(1)
C(16)	0.5074(2)	0.6440(3)	−0.1185(8)	5.0(1)
C(17)	0.5369(2)	0.6058(3)	−0.3141(7)	4.8(1)
C(18)	0.6017(2)	0.6431(3)	−0.3266(8)	5.1(1)
C(19)	0.6360(2)	0.6062(3)	−0.5108(7)	5.0(1)
C(20)	0.7009(2)	0.6454(3)	−0.5088(8)	5.3(1)
C(21)	0.7380(2)	0.6098(4)	−0.6871(8)	5.9(1)
C(22)	0.8014(2)	0.6520(4)	−0.6786(9)	8.1(2)

a) $B_{eq}=(8\pi^2/3)\sum\sum U_{ij}\, a_i^*\, a_j^*\, \boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

3.89(1), and N···N: 3.871(9) Å. A two-dimensional rectangular network of close contacts of antiparallel CN groups was observed for the plate crystal of 7OCB[3] (C···N; 3.41—3.64 Å) and higher homologues ($n\geq7$) of $HO(CH_2)_nOC_6H_4C_6H_4CN$[14] (C···N; 3.40—3.68 Å). Distances between carbonyloxy groups are also short (O(1)···O(2): 3.41(1) and O(1)···O(1): 3.519(3) Å).

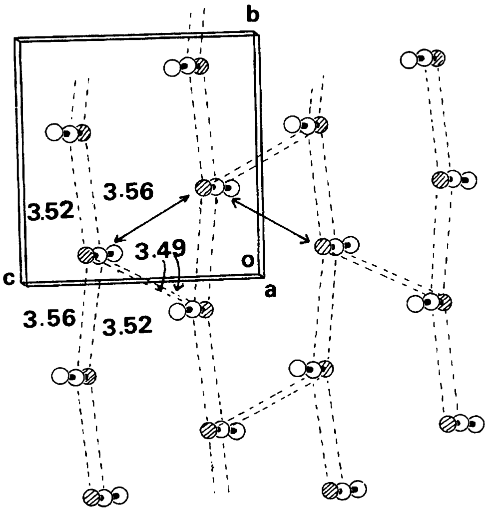

Fig. 7. Close contacts of CN groups in the crystal of 7OPCB. N–C(1)–C(2) moieties are shown. Arrows are the shortest distances between parallel CN groups (C···N: 3.77(2) Å).

Figure 8 shows the crystal structure of 8OPCB viewed along the *b* and *c* axes. In this case, a CN group is closely arranged to the carbonyloxy group (N···C(8): 3.585(6) Å) and one of the phenyl groups (C(1)···C(5): 3.563(6) Å) of a neighboring molecule with a parallel arrangements of the benzene rings. This is also regarded as a dimer structure. These dimers have an interdigitated structure as shown by the dot-and-dash lines, forming an alternate stacking of core moieties and chains. It is interpreted that this alternate stacking leads directly to a periodicity of density wave in a smectic structure on melting.

Relationships of the Crystal Structures and Mesophase Behavior. In contrast to the case of CP5OB, molecular long axes are parallel each other in all the crystals, as is expected from the fact that

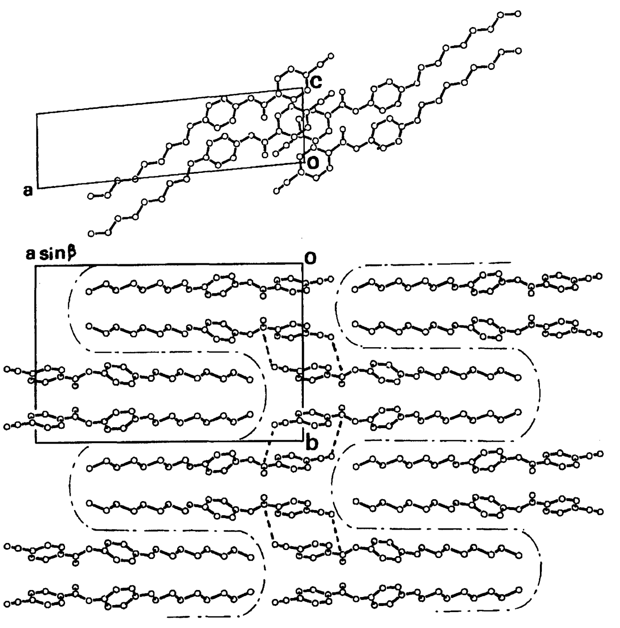

Fig. 8. Crystal structure of 8OPCB viewed along the *b* (upper) and *c* (lower) axes. Close contacts between CN and carbonyloxy groups are shown by broken lines. Dot-and-dash lines are drawn to show the periodicity of "layer" structure.

they are enantiotropic mesogens. Dimeric features are observed except for 7OPCB. This is also in conformity with the fact that the mesophases of both series are composed of dimers.[5] The dimers are formed with CN–CN interaction for CP6OB and CP8OB, but with CN-carbonyloxy interaction for 6OPCB and 8OPCB. However, no common features are observed with their homologues in the CP7OB and 7OPCB crystals. This fact may be related to an "odd–even" effect, although it is necessary to know structures of longer homologues to establish the effect. Nevertheless, the crystal structures of both series are closely related to the mesophase sequences; CP*n*OB and 6OPCB, which are nematogens, have imbricate structures of dimers, while 7OPCB and 8OPCB have smectic-like layer structures.

Cladis et al.[5] reported lengths of constituents in the nematic phase of *n*OPCB to be 31, 33.1, and 35.3 Å for $n=6$, 7, and 8, respectively, and the layer thickness of Sm A to be 34.2 ($n=7$), 35.3 ($n=8$), 37.0 ($n=9$), 38.3 ($n=10$), and 46.2 Å ($n=12$) at Sm A–nematic (for $n=7$, 8) or Sm A–isotropic transition (for $n\geq9$) for *n*OPCB. For the CP*n*OB series, only a length for $n=10$ was reported to be 33.1 Å in the nematic phase. From these data, they concluded that both series have a dimeric unit in the mesophases and the length of the dimer of CP10OB is shorter than that of 10OPCB. Furthermore, they proposed a model in which a dimer of *n*OPCB molecules was formed by association between the CN group and the O atom of the alkoxyl group on the basis of the *n*-dependence of the dimer lengths (Å), $d=16+2.58n$, probably assuming all-trans conformations for the chains.

Re-plotting their data, however, yields a better fit of the data, $d=20+1.9n$, which gives the length of a core moiety, i.e., a contribution except for a chain to be about 20 Å. The distance from O(3) to N in a molecule is 13 Å, as is schematically illustrated in Fig. 9. Thus, two core moieties are overlapped with the shift of about 7 Å, bringing the carbonyloxy and CN groups close. On the other hand, the difference of 5 Å between the dimer lengths of 10OPCB and CP10OB roughly agrees with the shift of the overlapped molecules shown in Fig. 9, suggesting that CP10OB molecules are associated with almost completely overlapped core moities in the nematic phase. The different dimer structures of the two series are related to the different magnitudes of dipole moments caused by opposite directions of the carbonyloxy group with respect to the CN group, as follows. In the *n*OPCB series, as the C=O group is conjugated to the benzene ring to which the CN group is attached, both of the electronegative groups attract electrons from each other, counterbalancing their dipole moments and hence reducing the overall dipole moment along the molecular long axis. For the CP*n*OB series, as the direction of the C=O group is opposite to that for *n*OPCB, dipole moments of CN and C=O groups along the molecular long axis are additive. A similar situation was studied[15] for 4-methoxybiphenyl-4′-yl 4-cyanobenzoate and 4-cyanophenyl 4-methoxybiphenyl-4′-carboxylate, for which total dipole moments were obtained by MNDO calculation to be 2.89 and 5.24 D, respectively. Thus, it is interpreted that when a longitudinal dipole moment is large enough, two antiparallel molecules are overlapped almost completely, while when it is not so large, molecules are overlapped only partly. Referring to these dimeric structures, it is pointed out that CN–carbonyloxy interaction, which is expected to form dimers in mesophases of the *n*OPCB series, is found in the crystals of 6OPCB and 8OPCB. On the other hand, any special interaction between CN and O atom of the alkoxyl group, which is regarded

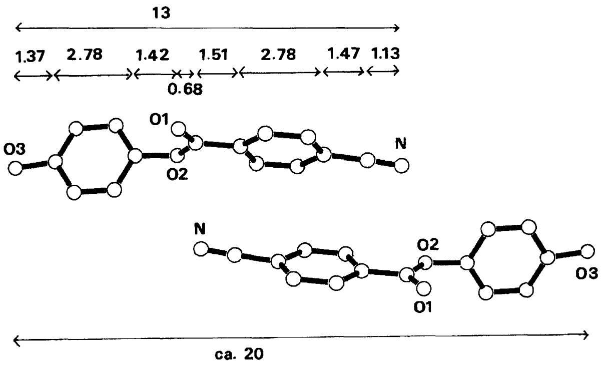

Fig. 9. A model proposed for overlapping of core moieties of *n*OPCB. The distances (Å) are average values for $n=6$, 7, and 8. Orientation around the molecular long axis is arbitrary.

to be responsible to the dimers in mesophases for the CP*n*OB series, is not found in these crystals of CP*n*OB. This is probably because more bulky and shorter dimer of CP*n*OB with a complete overlapping of core moieties than that of *n*OPCB would not be packed efficiently in the crystalline states. The lack of packing efficiency may be also responsible for the fact that this series shows much less tendency to have smectic phases than the counterpart series.

It is concluded that the crystal structures of two isomeric series of cyano esters show the characteristic features of the mesophases, i.e., dimerization which leads to imbricate structures for nematogens and smectic-like layer structures for smectogens. However, dimeric units, which are supposed to exist in the mesophases, are found only in the crystals of 6OPCB and 8OPCB, but not in the other series. This is interpreted to be due to packing efficiency of the different shapes of dimers, which leads to the different phase sequences of the two series.

This work was supported by a Grant-in-Aid from the Hayashi Memorial Foundation for Female Natural Scientists to K. H.

References

1) K. Ito, K. Endo, K. Hori, T. Nemoto, H. Uekusa, and Y. Ohashi, *Liq. Cryst.*, **17**, 747 (1994), and references cited therein.

2) K. Hori, Y. Koma, A. Uchida, and Y. Ohashi, *Mol. Cryst. Liq. Cryst.*, **225**, 15 (1993).

3) K. Hori, Y. Koma, M. Kurosaki, K. Itoh, H. Uekusa, Y. Takenaka, and Y. Ohashi, to be published.

4) J. W. Goodby, T. M. Leslie, P. E. Cladis, and P. L. Finn, "Liquid Crystals and Ordered Fluids," ed by A. C. Griffin and J. F. Johnson, Plenum Press, New York (1984), Vol. 4, p. 89.

5) It was reported[4)] that CP10OB has supercooled S_A, which transforms to nem. at the same temperature as the crystal melts to nem.

6) P. E. Cladis, P. L. Finn, and J. W. Goodby, "Liquid Crystals and Ordered Fluids," ed by A. C. Griffin and J. F. Johnson, Plenum Press, New York (1984), Vol. 4, p. 203.

7) U. Baumeister, H. Hartung, M. Gdaniec, and M. Jaskolski, *Mol. Cryst. Liq. Cryst.*, **69**, 119 (1981).

8) "teXsan, Crystal Structure Analysis Package," Molecular Structure Corporation (1985 & 1992).

9) G. M. Sheldrick, "SHELXL93, a program for the refinement of the crystal structure," University of Göttingen, Germany (1993).

10) "International Tables for Crystallography," ed by A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht (1992), Vol. C.

11) The tables for the bond lengths and angles, the anisotropic temperature factors for non-hydrogen atoms, atomic parameters for hydrogen atoms, and the $F_o - F_c$ are deposited as Document No. 68019 at the Office of the Editor of Bull. Chem. Soc. Jpn.

12) C. Johnson, "ORTEP, Report ORNL-3794," Oak Ridge National Laboratory, Tennessee (1965).

13) "Kagaku Binran, Kiso-hen," ed by the Chemical Society of Japan, Maruzen, Tokyo (1984), Vol. II, p. 722.

14) P. Zugenmaier and A. Heiske, *Liq. Cryst.*, **15**, 635 (1993).

15) H. Takeda, Y. Sakurai, S. Takenaka, H. Miyake, T. Doi, and S. Kusabayashi, *J. Chem. Soc.*, *Faraday Trans.*, **86**, 3429 (1990). Here, the former compound is a substitute of a S_A mesogen, 4-octyloxybiphenyl-4′-yl 4-cyanobenzoate and the latter is a substitute of a nematogen, 4-cyanophenyl 4-octyloxybiphenyl-4′-carboxylate.