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Crystal and Molecular Structure of a Cybotactic Nematic Compound bis(4′-n-Butoxybenzal—Chloro-1,4-Phenylinediamine

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Crystal and Molecular Structure of a Cybotactic Nematic Compound bis-(4′-*n*-Butoxybenzal)-2-Chloro-1,4-Phenylinediamine

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The crystal and molecular structure of a cybotactic nematic compound bis-(4′-*n*-butoxybenzal)-2-chloro-1,4-phenylinediamine (BOCP in short) has been reported. The crystals belong to monoclinic system with space group $P2_1/c$, $a = 36.693$, $b = 14.940$, $c = 6.1058$ Å, $\beta = 93.89°$ and $Z = 4$. The structure was determined by direct methods, with a final R-value of 0.049 ($R_w = 0.070$) for 1979 observed reflections. The molecules are almost in their extended conformation. The molecules are inclined to the *ab*-plane, the planar aromatic core region being almost parallel to the *ac*-plane. Molecular packing in relation to the liquid crystal phase is discussed.

Keywords: liquid crystal, cybotactic nematic, x-ray study, crystal structure, structure-property relationship

INTRODUCTION

The hexyl, octyl, decyl and dodecyl members of the homologous series of bis-(4′-*n*-alkoxybenzal)-2-chloro-1,4-phenylinediamine have been studied by x-ray diffraction[1–4] to ascertain the molecular model of the cybotactic nematic phase which they exhibit. It is suggested that in this phase the molecules are arranged in 'cybotactic groups' such that the ends of the rod like molecules constitute more or less a well defined boundary plane which makes an angle with the average direction of the molecules in the group. It is expected that the packing of the molecules in the crystal lattice may explain the occurrence of cybotactic nematic phase. A survey of the knowledge of the solid-mesophase relationship has been given by Bryan.[5] However this relationship is very complicated and any general conclusion should be treated with caution. Crystal structure of any cybotactic nematic precursor have

not been reported so far. We therefore undertook the structural study of the series and here we report the results on its eighth member (henceforth termed as BOCP).

From x-ray and texture studies we found[4] the transition temperatures (°C) of BOCP as follows:

$$\mathrm{Cr} \underset{53.4 - 56.4}{\overset{60.0 - 61.7}{\rightleftharpoons}} \mathrm{N_C} \underset{}{\overset{178.1 - 178.5}{\rightleftharpoons}} \mathrm{I}$$

EXPERIMENTAL

Needle shaped monoclinic cystals were obtained by slow evaporation from a solution of BOCP in acetone. Systematic absences of h0l reflections with l odd and of 0k0 reflections with k odd indicated that the space group is $P2_1/c$. The density measured by floatation technique (see Table I) revealed four molecules per unit cell. The cell parameters were refined by least-squares fit using accurate θ-measurements of 23 reflections with $50° < 2\theta < 58°$. 3352 unique reflections were measured on an Enraf Nonius CAD4 Diffractometer using graphite monochromated Cuk_α radiation, 1979 of which have $I \geq 2.5\sigma(I)$. Important crystallographic data are given in Table I.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by Direct Methods using the program SAPI.[6] Block diagonal least-squares refinement with 1979 observed reflections and with anistropic temperature factor for the non-hydrogen atoms and isotropic for the hydrogen atoms converged to $R = 0.049$ and $R_W = 0.070$ respectively. A weighting scheme $[W = (6.4 + F_{obs} + 0.0068F^2_{obs})^{-1}]$ and extinction correction was applied. Atomic scattering factors were taken from Stewart et al[7] for H and from Cromer and Waber[8] for the others. All calculations were carried out with the X-RAY System.[9]

TABLE I

Crystal data

Molecular Formula	C36 H47 N2 Cl O2
Molecular weight	575.20 gm/mol
Crystal system	Monoclinic
Space group	$P2_1/c$
a = 36.693(3) Å	
b = 14.940(1) Å	
c = 6.1058(6) Å	
β = 93.89 (1) °	
V = 3339.4 Å^3	
D_c = 1.14 gm/cm^3	
D_m = 1.15 gm/cm^3	
Z = 4	
λ(Cuk_α) = 1.5418 Å	
Number of independent reflections 3392	
Number of observed reflections	1979 (I ≥ 2.5 σ (I))

For least-squares planes and inter-molecular short contact calculations local programs were used. Final positional and thermal parameters are given in Tables II–IV. The labelling of the atoms is shown in Figure 1. Bond lengths and angles are given in Tables V and VI.

RESULTS AND DISCUSSIONS

Molecular Geometry and Conformation

Molecular structures of a number of benzylideneanilines have been reported[10] and a constant pattern of bond lengths and angles is found in the central region of

TABLE II

Fractional co-ordinates of the non-hydrogen atoms and equivalent isotropic thermal parameters

	X	Y	Z	Ueq
Cl(1)	0.23827(4)	-0.0041(1)	0.7711(3)	0.087(1)
C(1)	0.7499(2)	0.1572(5)	-0.302(1)	0.110(6)
C(2)	0.7122(2)	0.1174(4)	-0.3285(9)	0.074(4)
C(3)	0.6884(1)	0.1499(4)	-0.1533(9)	0.065(4)
C(4)	0.6499(1)	0.1124(3)	-0.1647(8)	0.059(3)
C(5)	0.6285(1)	0.1425(4)	0.0248(9)	0.066(4)
C(6)	0.5902(1)	0.1088(3)	0.0307(8)	0.058(3)
C(7)	0.5712(1)	0.1414(4)	0.2309(9)	0.065(4)
C(8)	0.5328(1)	0.1090(3)	0.2457(8)	0.056(3)
C(9)	0.4853(1)	0.1301(3)	0.4940(7)	0.050(3)
C(10)	0.4760(1)	0.1675(3)	0.6934(8)	0.055(3)
C(11)	0.4414(1)	0.1593(3)	0.7546(8)	0.056(3)
C(12)	0.4147(1)	0.1163(3)	0.6251(8)	0.054(3)
C(13)	0.4240(1)	0.0822(4)	0.4234(8)	0.065(4)
C(14)	0.4588(1)	0.0870(4)	0.3615(8)	0.063(3)
C(15)	0.3771(1)	0.1096(3)	0.6892(8)	0.060(3)
C(16)	0.3315(1)	0.1227(3)	0.9359(8)	0.055(3)
C(17)	0.3221(1)	0.1724(3)	1.1184(8)	0.059(3)
C(18)	0.2867(1)	0.1705(4)	1.1848(8)	0.061(3)
C(19)	0.2595(1)	0.1188(3)	1.0816(8)	0.055(3)
C(20)	0.2699(1)	0.0682(3)	0.9009(9)	0.061(3)
C(21)	0.3049(1)	0.0694(3)	0.8309(8)	0.062(3)
C(22)	0.2135(1)	0.1333(4)	1.3211(9)	0.065(4)
C(23)	0.1753(1)	0.1291(3)	1.3742(8)	0.057(3)
C(24)	0.1645(2)	0.1610(4)	1.5725(9)	0.071(4)
C(25)	0.1286(1)	0.1594(4)	1.6257(9)	0.070(4)
C(26)	0.1027(1)	0.1217(4)	1.4817(8)	0.063(3)
C(27)	0.1131(2)	0.0875(4)	1.2812(8)	0.076(4)
C(28)	0.1484(2)	0.0915(4)	1.2318(9)	0.074(4)
C(29)	0.0538(1)	0.1445(4)	1.7194(9)	0.070(4)
C(30)	0.0145(1)	0.1133(4)	1.7244(9)	0.067(4)
C(31)	-0.0028(1)	0.1418(4)	1.933(1)	0.072(4)
C(32)	-0.0414(1)	0.1106(4)	1.9435(9)	0.071(4)
C(33)	-0.0601(1)	0.1407(4)	2.145(1)	0.074(4)
C(34)	-0.0994(2)	0.1113(4)	2.154(1)	0.086(4)
C(35)	-0.1178(2)	0.1481(6)	2.348(1)	0.122(6)
C(36)	-0.1571(2)	0.1228(7)	2.352(2)	0.165(9)
N(1)	0.3677(1)	0.1303(3)	0.8773(7)	0.058(3)
N(2)	0.2226(1)	0.1145(3)	1.1314(7)	0.069(3)
O(1)	0.52076(9)	0.1433(2)	0.4494(5)	0.058(2)
O(2)	0.06620(9)	0.1143(3)	1.5146(6)	0.079(3)

TABLE III

Fractional co-ordinates and isotropic thermal parameters of the hydrogen atoms

	X	Y	Z	U
H(10)	0.494(1)	0.194(3)	0.773(7)	0.07(1)
H(11)	0.434(1)	0.190(3)	0.876(6)	0.05(1)
H(13)	0.404(1)	0.053(3)	0.333(7)	0.06(1)
H(14)	0.465(1)	0.067(3)	0.237(7)	0.08(2)
H(15)	0.360(1)	0.090(3)	0.586(6)	0.06(1)
H(17)	0.3465(8)	0.197(2)	1.222(5)	0.024(9)
H(18)	0.282(1)	0.212(3)	1.315(8)	0.09(2)
H(21)	0.309(1)	0.028(3)	0.713(7)	0.07(1)
H(22)	0.231(2)	0.147(4)	1.44(1)	0.13(2)
H(24)	0.182(1)	0.184(3)	1.668(7)	0.07(1)
H(25)	0.122(1)	0.185(3)	1.750(8)	0.09(2)
H(27)	0.094(1)	0.059(3)	1.200(6)	0.05(1)
H(28)	0.157(1)	0.066(3)	1.097(8)	0.09(2)
H(31)	0.702(1)	0.132(3)	0.004(7)	0.08(2)
H(32)	0.685(1)	0.215(3)	-0.161(7)	0.08(1)
H(41)	0.637(1)	0.129(3)	-0.302(7)	0.08(1)
H(42)	0.653(1)	0.046(3)	-0.169(6)	0.05(1)
H(51)	0.641(1)	0.131(3)	0.153(8)	0.09(2)
H(52)	0.630(1)	0.212(4)	0.046(9)	0.11(2)
H(61)	0.573(1)	0.130(2)	-0.099(6)	0.05(1)
H(62)	0.590(1)	0.042(2)	0.025(6)	0.05(1)
H(71)	0.588(1)	0.122(3)	0.371(7)	0.07(1)
H(72)	0.573(1)	0.207(3)	0.257(7)	0.08(2)
H(81)	0.517(1)	0.132(3)	0.121(8)	0.09(2)
H(82)	0.5312(9)	0.041(2)	0.248(6)	0.04(1)
H(101)	0.749(1)	0.229(4)	-0.315(8)	0.11(2)
H(102)	0.765(1)	0.140(4)	-0.134(9)	0.12(2)
H(103)	0.762(1)	0.145(3)	-0.417(8)	0.09(2)
H(201)	0.699(1)	0.133(3)	-0.478(7)	0.08(2)
H(202)	0.710(1)	0.049(3)	-0.329(7)	0.07(1)
H(291)	0.069(1)	0.115(3)	1.851(8)	0.09(2)
H(292)	0.054(1)	0.216(3)	1.733(8)	0.08(2)
H(301)	-0.001(1)	0.142(3)	1.597(7)	0.08(2)
H(302)	0.015(1)	0.044(3)	1.716(8)	0.10(2)
H(311)	0.015(1)	0.122(3)	2.060(7)	0.07(1)
H(312)	-0.003(1)	0.208(3)	1.939(6)	0.06(1)
H(321)	-0.059(1)	0.132(3)	1.821(8)	0.08(2)
H(322)	-0.042(1)	0.039(3)	1.943(8)	0.08(2)
H(331)	-0.046(1)	0.115(3)	2.286(7)	0.08(2)
H(332)	-0.060(1)	0.207(3)	2.142(7)	0.07(1)
H(341)	-0.116(1)	0.125(4)	2.026(9)	0.12(2)
H(342)	-0.102(1)	0.041(4)	2.154(9)	0.11(2)
H(351)	-0.103(2)	0.144(4)	2.49(1)	0.14(2)
H(352)	-0.120(2)	0.226(5)	2.33(1)	0.17(3)
H(361)	-0.171(2)	0.141(5)	2.17(1)	0.18(3)
H(362)	-0.161(2)	0.058(5)	2.31(1)	0.17(3)
H(363)	-0.167(2)	0.156(5)	2.46(1)	0.17(3)

these molecules. Intra-molecular steric repulsions cause the angles C—C=N and two C—C—N connected to two benzene rings to be enlarged from 120°, and the angles C=N—C and the other two C—C—N to be reduced. The observed bond lengths and angles conform to this pattern.

In the benzylidene rings the pattern of bond distances is similar to that found in *p*-[(*p'*-ethoxybenzylidene)amino] benzonitrile[10] with marked shortening of C10–

TABLE IV

Anisotropic thermal parameters of the non-hydrogen atoms. The temperature factor is of the form $\exp[-2\pi^2 (U11.h^2.a^{*2} + U22.k^2.b^{*2} + U33.l^2.c^{*2} + 2U12.h.k.a^*.b^* + 2U13.h.l.a^*.c^* + 2U23.k.l.b^*.c^*)]$

	U11	U22	U33	U12	U13	U23
Cl(1)	0.0712(9)	0.107(1)	0.085(1)	-0.014(1)	0.0039(8)	-0.032(1)
C(1)	0.085(5)	0.136(6)	0.113(6)	-0.003(4)	0.037(4)	-0.016(5)
C(2)	0.074(4)	0.078(4)	0.071(4)	-0.003(3)	0.017(3)	-0.006(3)
C(3)	0.067(4)	0.064(4)	0.066(4)	0.007(3)	0.018(3)	0.001(3)
C(4)	0.064(3)	0.057(3)	0.058(3)	0.010(3)	0.007(3)	-0.002(3)
C(5)	0.057(3)	0.073(4)	0.068(4)	-0.002(3)	0.001(3)	-0.009(3)
C(6)	0.053(3)	0.057(3)	0.063(3)	0.002(3)	0.000(3)	-0.003(3)
C(7)	0.067(4)	0.066(4)	0.063(3)	-0.006(3)	0.007(3)	-0.011(3)
C(8)	0.061(3)	0.051(3)	0.055(3)	-0.007(3)	-0.002(3)	-0.002(3)
C(9)	0.054(3)	0.042(3)	0.055(3)	0.003(2)	0.003(3)	0.002(2)
C(10)	0.063(3)	0.048(3)	0.055(3)	-0.003(3)	0.000(3)	-0.006(3)
C(11)	0.069(3)	0.051(3)	0.048(3)	0.003(3)	-0.001(3)	-0.004(3)
C(12)	0.053(3)	0.058(3)	0.051(3)	0.001(3)	0.006(3)	0.004(3)
C(13)	0.056(3)	0.087(4)	0.053(3)	-0.014(3)	0.006(3)	-0.011(3)
C(14)	0.066(3)	0.070(4)	0.053(3)	-0.004(3)	0.008(3)	-0.009(3)
C(15)	0.067(3)	0.057(3)	0.054(3)	0.001(3)	-0.002(3)	-0.006(3)
C(16)	0.065(3)	0.047(3)	0.052(3)	0.000(3)	0.002(3)	0.004(3)
C(17)	0.070(4)	0.057(3)	0.050(3)	0.002(3)	0.014(3)	0.004(3)
C(18)	0.069(4)	0.062(3)	0.053(3)	-0.005(3)	0.013(3)	-0.008(3)
C(19)	0.071(3)	0.048(3)	0.050(3)	0.002(3)	0.015(3)	0.002(3)
C(20)	0.066(3)	0.054(3)	0.062(3)	-0.003(3)	-0.002(3)	0.005(3)
C(21)	0.070(4)	0.055(3)	0.062(3)	0.007(3)	0.009(3)	-0.012(3)
C(22)	0.070(4)	0.063(4)	0.063(4)	-0.003(3)	0.007(3)	0.001(3)
C(23)	0.065(3)	0.058(3)	0.050(3)	0.000(3)	0.009(3)	0.004(3)
C(24)	0.064(4)	0.083(4)	0.065(4)	-0.016(3)	0.002(3)	-0.014(3)
C(25)	0.071(4)	0.069(4)	0.071(4)	-0.009(3)	0.006(3)	-0.017(3)
C(26)	0.056(3)	0.071(4)	0.062(3)	-0.010(3)	0.009(3)	0.004(3)
C(27)	0.074(4)	0.109(5)	0.046(3)	-0.023(4)	0.002(3)	-0.017(3)
C(28)	0.070(4)	0.098(5)	0.055(4)	-0.008(3)	0.006(3)	-0.004(3)
C(29)	0.067(4)	0.080(4)	0.064(4)	0.005(3)	0.016(3)	-0.004(3)
C(30)	0.056(3)	0.071(4)	0.074(4)	0.002(3)	0.004(3)	0.006(3)
C(31)	0.058(3)	0.066(4)	0.094(5)	0.008(3)	0.006(3)	-0.005(3)
C(32)	0.052(3)	0.075(4)	0.087(4)	0.005(3)	0.005(3)	-0.001(3)
C(33)	0.066(4)	0.067(4)	0.091(4)	0.004(3)	0.016(3)	-0.009(3)
C(34)	0.066(4)	0.092(5)	0.103(5)	-0.008(4)	0.025(3)	-0.005(4)
C(35)	0.081(5)	0.147(7)	0.143(7)	-0.026(5)	0.041(5)	-0.053(6)
C(36)	0.097(6)	0.186(9)	0.22(1)	-0.020(6)	0.058(7)	-0.046(9)
N(1)	0.065(3)	0.056(3)	0.056(3)	0.001(2)	0.013(2)	-0.004(2)
N(2)	0.070(3)	0.078(3)	0.060(3)	-0.003(3)	0.017(2)	0.001(3)
O(1)	0.056(2)	0.067(2)	0.052(2)	-0.001(2)	0.001(2)	-0.006(2)
O(2)	0.060(2)	0.114(3)	0.064(2)	-0.009(2)	0.007(2)	-0.004(2)

C11 (or C27–C28) bond trans to C9–O1 (or C26–O2) and on the opposite side of the molecule from the alkyl substituent indicating a semi-quinodal character. Both the benzylidene rings have the —N=CH— and —O—CH_2— bonds trans with respect to the 1,4 axes. However, the average bond lengths of the two benzylidene rings are 1.378 Å and 1.379 Å and that of the aniline ring is 1.391 Å. They agree well with the expected values.[11]

The average C—C bond length in the chain parts is 1.509 Å and the average angle in the chain is 114.1°. Similar values are found in other mesogens.[12,13]

The overall molecular conformation of BOCP may be described with respect to

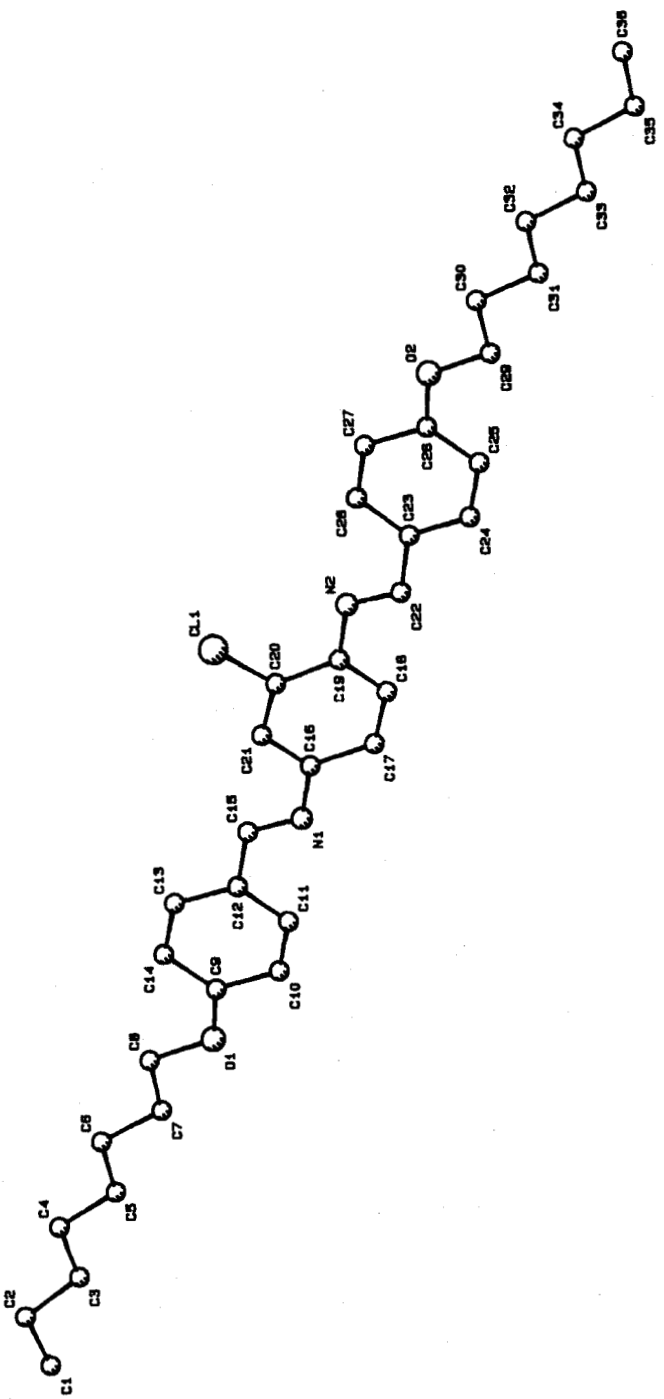

FIGURE 1 Perspective view of BOCP molecule.

TABLE V

Bond distance of the non-hydrogen atoms (Å) with standard deviations in parenthesis

C(1)	-	C(2)	1.503(9)	C(18)	-	C(19)	1.378(7)
C(2)	-	C(3)	1.506(8)	C(19)	-	C(20)	1.411(7)
C(3)	-	C(4)	1.517(7)	C(19)	-	N(2)	1.409(7)
C(4)	-	C(5)	1.510(7)	C(20)	-	C(21)	1.384(7)
C(5)	-	C(6)	1.497(7)	C(22)	-	C(23)	1.462(7)
C(6)	-	C(7)	1.527(8)	C(22)	-	N(2)	1.258(7)
C(7)	-	C(8)	1.499(7)	C(23)	-	C(24)	1.383(8)
C(8)	-	O(1)	1.443(6)	C(23)	-	C(28)	1.388(7)
C(9)	-	C(10)	1.403(7)	C(24)	-	C(25)	1.378(8)
C(9)	-	C(14)	1.382(7)	C(25)	-	C(26)	1.372(7)
C(9)	-	O(1)	1.361(6)	C(26)	-	C(27)	1.404(8)
C(10)	-	C(11)	1.352(7)	C(26)	-	O(2)	1.371(6)
C(11)	-	C(12)	1.378(7)	C(27)	-	C(28)	1.353(8)
C(12)	-	C(13)	1.397(7)	C(29)	-	C(30)	1.516(7)
C(12)	-	C(15)	1.461(7)	C(29)	-	O(2)	1.433(7)
C(13)	-	C(14)	1.358(7)	C(30)	-	C(31)	1.524(8)
C(15)	-	N(1)	1.260(7)	C(31)	-	C(32)	1.497(8)
C(16)	-	C(17)	1.401(7)	C(32)	-	C(33)	1.519(8)
C(16)	-	C(21)	1.382(7)	C(33)	-	C(34)	1.511(8)
C(16)	-	N(1)	1.405(6)	C(34)	-	C(35)	1.51(1)
C(17)	-	C(18)	1.387(7)	C(35)	-	C(36)	1.49(1)

various planar parts: plane (1) of the first benzylidene ring C9–C14, plane (2) of the aniline ring C16–C21, plane (3) of the second benzylidene ring C23–C28, planes of the groups C12–C15–N1–C16 (plane 4) and C19–N2–C22–C23 (plane 5), planes through the chain parts C1 to O1 (plane 6) and O2 to C36 (plane 7). Planes (1), (2), (3), (4) and (5) are planar within 0.01 Å and the chains are planar within 0.07 Å and 0.09 Å respectively. The interplanar angles between successive planes in the string 7-3-5-2-4-1-6 are 9,10, −23,20, −10, −6° respectively. The overall appearance of the molecule is approximately planar because the larger angles have alternating signs. As a result the molecule is in its most extended conformation with a molecular length of 39.4 Å.

Molecular Packing in Relation to the Liquid Crystalline Phase

Crystal structure of BOCP projected in *ab*-plane is shown in Figure 2 and the projection *ac*-plane in Figure 3. The molecules are inclined to the *ab*-plane at an angle of about 25°, the aromatic core region being almost parallel to the *ac*-plane. The molecules as a whole are almost parallel to the *a*-axis. This parallel imbricated mode of packing in the crystal gives rise to a nematic phase on melting.

All inter-molecular contact distances less than 3.8 Å involving non-hydrogen atoms are listed in Table VII. It is found that there are non-bonded interactions between molecules related by centers of inversion and molecules translated along *c*-axis. In this region two inter-molecular Cl–C distances are equal to the sum of their van der Waals' radii. Such non-bonded contacts also exist between molecules related by glide planes. Crystal structure of BOCP may, therefore, be described as molecules related by centers of inversion form layers in the *ac*-plane and these layers are stacked along the *b*-axis. Within the layers molecules are parallel and tilted to the *ab*-plane and neighbouring layers are related by a glide plane.

That the inter-layer interactions also exist in the nematic phase is revealed by

TABLE VI

Bond angles of the non-hydrogen atoms with standard deviations in parentheses

C(1)	-	C(2)	-	C(3)	111.7(5)
C(2)	-	C(3)	-	C(4)	115.6(4)
C(3)	-	C(4)	-	C(5)	112.7(4)
C(4)	-	C(5)	-	C(6)	117.1(4)
C(5)	-	C(6)	-	C(7)	113.0(4)
C(6)	-	C(7)	-	C(8)	115.2(4)
C(7)	-	C(8)	-	O(1)	106.4(4)
C(10)	-	C(9)	-	C(14)	119.4(4)
C(10)	-	C(9)	-	O(1)	114.1(4)
C(14)	-	C(9)	-	O(1)	126.5(4)
C(9)	-	C(10)	-	C(11)	119.5(4)
C(10)	-	C(11)	-	C(12)	122.0(5)
C(11)	-	C(12)	-	C(13)	117.9(5)
C(11)	-	C(12)	-	C(15)	121.8(4)
C(13)	-	C(12)	-	C(15)	120.3(4)
C(12)	-	C(13)	-	C(14)	121.2(5)
C(9)	-	C(14)	-	C(13)	120.0(5)
C(12)	-	C(15)	-	N(1)	123.3(5)
C(17)	-	C(16)	-	C(21)	118.0(5)
C(17)	-	C(16)	-	N(1)	116.6(4)
C(21)	-	C(16)	-	N(1)	125.3(5)
C(16)	-	C(17)	-	C(18)	120.5(5)
C(17)	-	C(18)	-	C(19)	122.7(5)
C(18)	-	C(19)	-	C(20)	115.6(5)
C(18)	-	C(19)	-	N(2)	127.0(5)
C(20)	-	C(19)	-	N(2)	117.3(4)
C(19)	-	C(20)	-	C(21)	122.7(5)
C(16)	-	C(21)	-	C(20)	120.3(5)
C(23)	-	C(22)	-	N(2)	120.9(5)
C(22)	-	C(23)	-	C(24)	121.0(5)
C(22)	-	C(23)	-	C(28)	122.0(5)
C(24)	-	C(23)	-	C(28)	117.1(5)
C(23)	-	C(24)	-	C(25)	122.3(5)
C(24)	-	C(25)	-	C(26)	119.3(5)
C(25)	-	C(26)	-	C(27)	119.3(5)
C(25)	-	C(26)	-	O(2)	125.6(5)
C(27)	-	C(26)	-	O(2)	115.1(4)
C(26)	-	C(27)	-	C(28)	120.0(5)
C(23)	-	C(28)	-	C(27)	121.9(5)
C(30)	-	C(29)	-	O(2)	106.3(4)
C(29)	-	C(30)	-	C(31)	112.5(4)
C(30)	-	C(31)	-	C(32)	113.4(5)
C(31)	-	C(32)	-	C(33)	115.0(5)
C(32)	-	C(33)	-	C(34)	115.2(5)
C(33)	-	C(34)	-	C(35)	113.6(5)
C(34)	-	C(35)	-	C(36)	113.9(7)
C(15)	-	N(1)	-	C(16)	122.3(4)
C(19)	-	N(2)	-	C(22)	120.5(4)
C(8)	-	O(1)	-	C(9)	116.3(3)
C(26)	-	O(2)	-	C(29)	118.3(4)

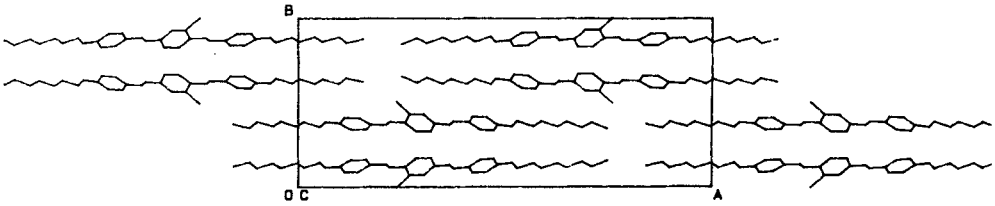

FIGURE 2 Crystal structure of BOCP in *ab*-plane.

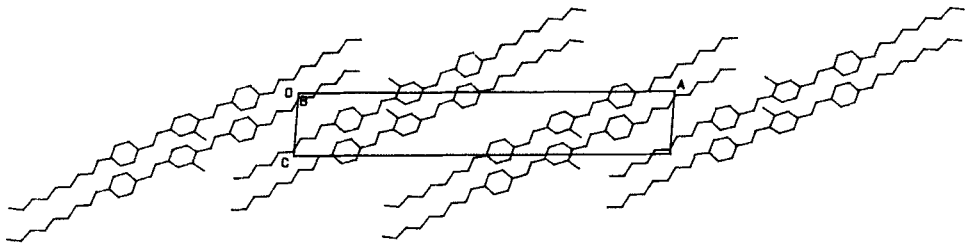

FIGURE 3 Crystal structure of BOCP in *ac*-plane.

TABLE VII

Intermolecular contact distances less then 3.8 Å involving non-hydrogen atoms only

Cl–Cl[a]	3.714	Cl–C2[a]	3.760	Cl–C22[b]	3.500
Cl–C23[b]	3.796	Cl–C24[b]	3.799	Cl–C36[f]	3.500
C4–C21[c]	3.718	C8–C13[c]	3.784	C8–C14[c]	3.784
C9–C10[d]	3.542	C9–C11[d]	3.783	C9–C11[e]	3.783
C10–O1[e]	3.575	C10–C9[e]	3.542	C14–O1[e]	3.690
C16–C17[d]	3.627	C16–C17[e]	3.627	C16–C18[d]	3.776
C16–C18[e]	3.707	C17–N1[e]	3.692	C17–C18[d]	3.707
C17–C18[e]	3.707	C23–C24[d]	3.645	C23–C24[e]	3.645

None: x, y, z; a: 1 − x, −y, −z; b: x, y, z − 1; c: 1 − x, −y, 1 − z; d: x, 1/2 − y, 1/2 + z − 1; e: x, 1/2 − y, 1/2 + z; f: −x, −y, 3 − z.

the following fact. In the x-ray diffraction photograph of the cybotactic nematic phase an equatorial diffraction ring appears[4] at an angle of about 5°, apart from the ring which usually arises due to inter-molecular interactions (Figure 4). In the crystal structure the distance between two chlorine atoms of molecules related by glide symmetry is on the average 8 Å. An interaction between chlorine atoms of 8 Å separation corresponds to diffraction ring at about 5° for the cybotactic nematic phase. This additional diffraction ring in the equatorial section does not appear in the diffraction photograph of the cybotactic nematic phase of OOBPD[14] since no chlorine atoms are present in these molecules which are otherwise the same as BOCP. Existence of this type of inter-layer interactions might be responsible for the occurrence of cybotactic nematic phase. Any definite conclusion can be made when crystal structures of other members of the series are determined.

Another interesting point to note is that the melting (143°C) and clearing point (231°C) of OOBPD is much higher than that of BOCP. Moreover it exhibits four

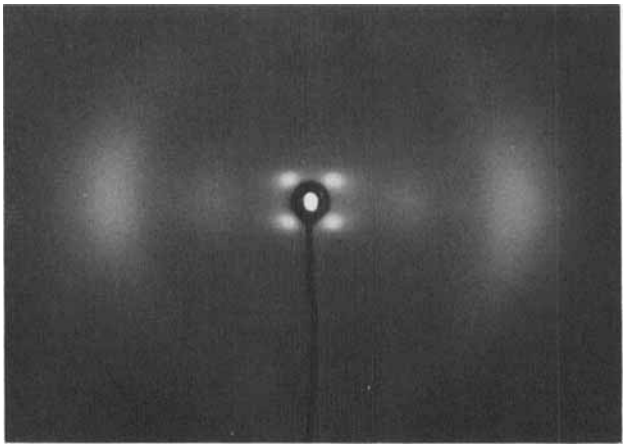

FIGURE 4 X-ray diffraction photograph of aligned BOCP sample in cybotactic nematic phase (83°C).

smectic phases. Stronger inter-molecular interactions in the aromatic region of the molecules in absence of the spacer chlorine atom and more efficient packing of the end chains might well be responsible for this.

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