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Crystal and Molecular Structure of 4′-Cyanophenyl-4-*n*-Butoxybenzoate

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The crystal and molecular structure of 4′-cyanophenyl-4-*n*-butoxybenzoate, which exhibits a monotropic nematic phase, has been determined using single crystal X-ray diffraction data. The crystals belong to the orthorhombic system, Pccn, a = 35.872 (8) Å, b = 11.331 (3) Å, c = 7.773 (2) Å, Z = 8. The structure has been solved by direct methods and refined to an R-value of 0.0502 with $F_0 > 2\sigma(F_0)$. The molecular structure shows that the butoxy group is extended in the gauche-conformation. The long molecular axes are arranged parallel to [100] and lie in y ≈ 0.11, 0.39, 0.61 and 0.89. In addition to that, the molecules are arranged in layers which are perpendicular to the a-axis have a thickness of a/2 (≈ 18 Å). Cyano-cyano contacts, N...N′ ≈ 3.54 Å, are found.

Keywords: Liquid crystal, crystal structure, molecular structure

INTRODUCTION

The crystal and molecular structure determination of materials which exhibit liquid crystalline phases is still an interesting subject. It is a valuable source of information about molecular conformation, molecular arrangement and intermolecular interactions as well. There have been many attempts[1–14] to find and understand the relation between the crystal and liquid crystal structures.

As a continuation of our X-ray investigations, with respect to the above mentioned aspects, we present in this work the X-ray structural determination of 4′-cyanophenyl-4-*n*-butoxybenzoate (CPBOB). This compound is of a particular interest because the next compound of its homologues series, namely 4′-cyanophenyl-4-*n*-pentoxybenzoate (CPPOB),[1] was found to posses high molecular symmetry (all the molecules are located in the mirror symmetry planes). Whereas such high symmetry was not found in the case of the closely related compound 4′-cyanophenyl-4-*n*-pentylbenzoate (CPPB).[3] On the other hand, CPBOB compound exhibits phase transitions similar to those of CPPOB[1] and CPPB.[3] Only a monotropic nematic phase is observed in the thermograms of these compounds, and the following is the thermal behavior of CPBOB:

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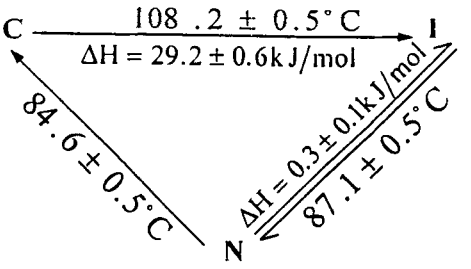

CRYSTAL DATA

The compound investigated (ZLI 2135) was provided by E. Merck, Darmstadt, Germany. Colorless crystals (plates) of CPBOB suitable for X-ray analysis were obtained by slow evaporation of the dissolved compound in an acetone solution. Intensity measurements were carried out at 25°C using a STOE-STADI-4 four-circle diffractometer with graphite monochromatized CuK_α-radiation ($\lambda = 1.54178$ Å). The lattice dimensions were determined by a least-squares refinement of 48 strong reflections within $74.3° < 2\theta < 76.7°$. The crystal data are given in Table I.

A crystal of size $0.4 \times 0.4 \times 0.6\ mm^3$ was used for the data collection. A total number of 4501 reflections were measured in the range $3° < 2\theta < 119°$ (scan $2\theta : \omega = 1:1$) leading to 2321 independent reflections of which 2286 had $F_0 > 2\sigma(F_0)$. The standard intensities ($11\bar{5}0, 1104, 1620$) were monitored every 90 min and the variation during the measurements was ± 2%. Lorentz, polarization and absorption corrections were performed.

STRUCTURE DETERMINATION

The structure of CPBOB was solved by direct methods using the program package SHELX-86,[15] which led to the positions of all non-hydrogen atoms. By consideration of

TABLE I

Crystal data

Molecular formula	$C_{18}H_{17}NO_3$
Molar mass ($g.mol^{-1}$)	298.34
Crystal system	Orthorhombic
Space group	Pccn
No. of Int. Tab.	56
a(Å)	35.872(8)
b(Å)	11.331(3)
c(Å)	7.773(2)
V($Å^3$)	3159.4
Z	8
D_c($g.cm^{-3}$)	1.24
μ[CuKα](cm^{-1})	6.06
F(000)	1248
Independent reflections	2321
Unobserved reflections	($F_0 < 2\sigma(F_0)$) 35
R [R_w, where $w = 1/\sigma^2(F_0)$]	0.0502(0.0516)

TABLE II

Positional and anisotropic thermal parameters for the non-hydrogen atoms with e.s.d.'s in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	0.7646(1)	0.8994(2)	0.1800(5)	0.0421(14)	0.1231(22)	0.2158(36)	0.0510(23)	−0.0018(17)	−0.0076(13)
C(1)	0.7330(1)	0.8959(2)	0.1725(4)	0.0477(15)	0.0804(18)	0.1188(25)	0.0243(17)	0.0023(15)	−0.0045(13)
C(2)	0.6928(1)	0.8965(2)	0.1672(3)	0.0384(11)	0.0647(14)	0.0702(16)	0.0041(12)	0.0030(11)	−0.0036(10)
C(3)	0.6750(1)	0.9853(2)	0.0775(3)	0.0480(13)	0.0794(16)	0.0845(19)	0.0272(15)	0.0010(13)	−0.0120(11)
C(4)	0.6365(1)	0.9922(2)	0.0783(3)	0.0494(13)	0.0694(15)	0.0781(18)	0.0209(13)	−0.0076(12)	−0.0034(11)
C(5)	0.6167(1)	0.9094(2)	0.1690(3)	0.0342(11)	0.0577(13)	0.0612(14)	−0.0081(11)	0.0040(10)	−0.0012(9)
C(6)	0.6338(1)	0.8193(2)	0.2555(3)	0.0453(12)	0.0573(13)	0.0808(17)	0.0131(13)	0.0143(12)	−0.0007(10)
C(7)	0.6723(1)	0.8131(2)	0.2543(3)	0.0454(13)	0.0643(14)	0.0848(18)	0.0182(13)	0.0080(12)	0.0063(10)
O(1)	0.5780(0)	0.9261(1)	0.1823(2)	0.0358(8)	0.0589(9)	0.0831(11)	−0.0145(8)	0.0018(8)	−0.0001(6)
C(8)	0.5552(1)	0.8451(2)	0.1065(3)	0.0409(11)	0.0581(13)	0.0612(15)	−0.0080(12)	0.0028(11)	0.0008(10)
O(2)	0.5670(0)	0.7658(2)	0.0204(3)	0.0454(9)	0.0996(13)	0.1084(15)	−0.0544(12)	0.0125(9)	0.0014(9)
C(9)	0.5157(0)	0.8662(2)	0.1469(3)	0.0373(10)	0.0511(12)	0.0486(13)	−0.0015(10)	0.0017(9)	0.0030(9)
C(10)	0.5035(1)	0.9593(2)	0.2469(3)	0.0422(11)	0.0479(11)	0.0583(14)	−0.0045(11)	−0.0003(10)	−0.0014(9)
C(11)	0.4661(1)	0.9719(2)	0.2900(3)	0.0440(11)	0.0477(12)	0.0612(14)	−0.0062(10)	0.0000(10)	0.0071(9)
C(12)	0.4408(1)	0.8882(2)	0.2305(3)	0.0344(10)	0.0567(12)	0.0515(13)	−0.0005(10)	−0.0027(9)	0.0066(9)
C(13)	0.4526(1)	0.7968(2)	0.1249(3)	0.0407(11)	0.0665(14)	0.0651(15)	−0.0197(12)	−0.0024(11)	−0.0018(10)
C(14)	0.4897(1)	0.7858(2)	0.0832(3)	0.0425(11)	0.0631(14)	0.0613(15)	−0.0179(12)	0.002(10)	0.0030(10)
O(3)	0.4039(0)	0.8870(1)	0.2695(2)	0.0351(8)	0.0725(10)	0.0690(11)	−0.0164(8)	0.0019(7)	0.0059(7)
C(15)	0.3894(1)	0.9759(2)	0.3842(4)	0.0483(13)	0.0658(14)	0.0886(19)	−0.0168(14)	0.0104(13)	0.0095(11)
C(16)	0.3484(1)	0.9508(2)	0.4079(4)	0.0459(13)	0.0804(17)	0.0872(19)	−0.0111(15)	0.0103(13)	0.0120(12)
C(17)	0.3401(1)	0.8371(2)	0.4969(4)	0.0681(17)	0.0877(19)	0.0915(21)	−0.0069(17)	0.0159(15)	0.0037(14)
C(18)	0.2983(1)	0.8183(3)	0.5261(5)	0.0783(19)	0.1032(22)	0.1251(28)	−0.0175(21)	0.0335(20)	−0.0173(17)

the anisotropic thermal factors and geometrically idealized H-positions related to their respective carbon atoms (C—H = 1.080 Å), as well as fixed isotropic thermal factors for the hydrogen atoms (fixed at 1.1 times that of the connecting carbon atoms), the final refinement converged at $R = 0.0502$ ($R_w = 0.0516$, where $w = 1/\sigma^2(F_0)$).

Positional and anisotropic thermal parameters for the non-hydrogen atoms are listed in Table II. Lists of the observed and calculated structure factors, and the positional parameters for the hydrogen atoms are available from the authors on request.

Molecular Structure

The molecular structure of CPBOB is shown in Figure 1. It shows that the butoxy group is extended in the gauche-conformation. Selected bond lengths and angles are

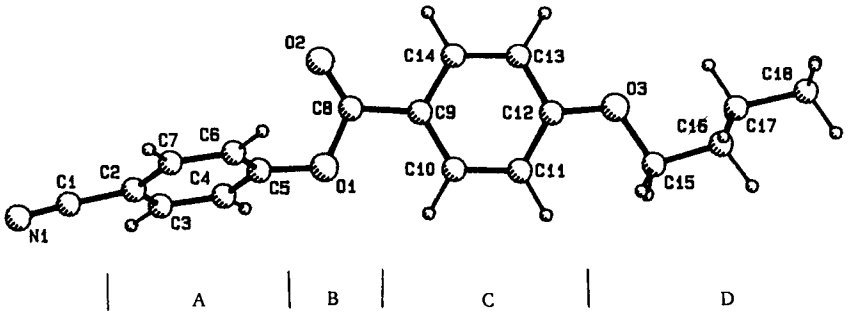

FIGURE 1 CPBOB molecule.

TABLE III

Selected bond lengths (Å) and angles (°) with e.s.d.'s in parentheses, and dihedral angles (°) (labelling of planes according to Figure 1)

Ring 1	C(2)...C(7)	C—C	1.377(5)
Ring 2	C(9)...C(14)	C—C	1.386(5)
N(1)—C(1)	1.135(3)	C(8)—O(2)	1.197(2)
C(1)—C(2)	1.444(3)	C(8)—C(9)	1.473(3)
C(5)—O(1)	1.404(2)	C(12)—O(3)	1.361(2)
C(8)—O(1)	1.363(2)	O(3)—C(15)	1.441(2)
C(15)—C(16)	1.510(3)	C(16)—C(17)	1.493(3)
Ring 1 C—C—C	120.0(10)		
Ring 2 C—C—C	120.0(7)		
O(2)—C(8)—O(1)	122.3(2)		
O(1)—C(8)—C(9)	112.1(2)		
O(2)—C(8)—C(9)	125.6(2)		
C(8)—O(1)—C(5)	118.0(2)		
N(1)—C(1)—C(2)	177.4(3)		
C(12)—O(3)—C(15)	118.8(2)		
O(3)—C(15)—C(16)	107.2(2)		
C(15)—C(16)—C(17)	114.4(2)		
C(16)—C(17)—C(18)	112.5(2)		
A/B 70.3	A/C 69.6	B/C 4.8	C/D 32.6

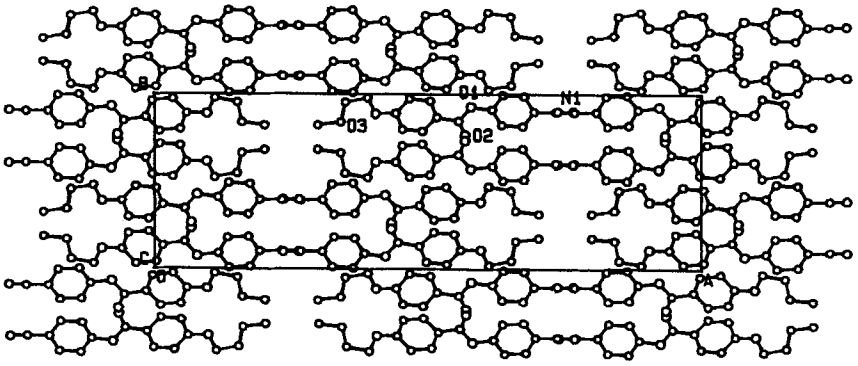

FIGURE 2 CPBOB, viewed along the c-axis.

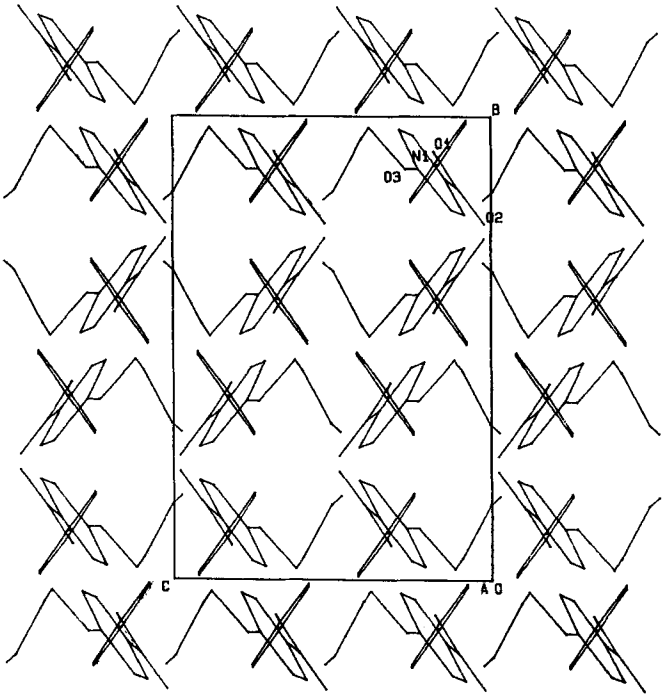

FIGURE 3 CPBOB, viewed along the a-axis.

given in Table III. All these values are found to be of normal order of magnitudes, as compared with their corresponding values for CPPOB[1] and CPPB.[3] The dihedral angles between best planes of different parts of the molecule are also given in Table III. For the A/B and B/C angles extreme values of 90° and 0°, respectively, were found in the case of CPPOB.[1]

Molecular Packing

The packing of CPBOB molecules in the solid crystalline state is shown in Figures 2 and 3. The molecules are packed parallel to the long crystallographic a-axis, where the molecular long axes are along N(1), C(1), C(2), C(5) and C(12), and lie in $y \approx 0.11, 0.39, 0.61$ and 0.89.

There is one type of layers perpendicular to [100] and have a thickness of $a/2 \approx 18$ Å (molecular length). Coupling between layers is due to cyano-cyano contacts ($N \ldots N' \approx 3.54$ Å) respectively through van der Waals interactions.

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