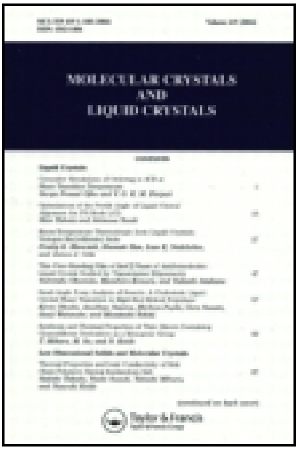

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Crystal and Molecular Structure of the Nematogenic Compound 4′-Cyanophenyl-4-n-Pentoxybenzoate

U. Baumeister [a] , H. Hartung [a] , M. Gdaniec [b] & M. Jaskólski [b]

[a] Sektion Chemie, Martin-Luther-Universität Halle, GDR, Mühlforte 1, DDR-402, Halle

[b] Institute of Chemistry, Adam Mickiewicz University, ul. Grunwaldzka 6, 60-780, Poznań, Poland

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Crystal and Molecular Structure of the Nematogenic Compound 4′-Cyanophenyl-4-*n*-Pentoxybenzoate

U. BAUMEISTER and H. HARTUNG

Sektion Chemie, Martin-Luther-Universität Halle, GDR, Mühlforte 1, DDR-402 Halle.

and

M. GDANIEC and M. JASKÓLSKI

Institute of Chemistry, Adam Mickiewicz University,
ul. Grunwaldzka 6, 60–780 Poznań, Poland.

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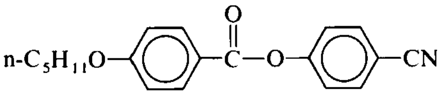
The title compound with the formula $C_5H_{11}O$-C_6H_4-COO-C_6H_4-CN (CPPOB) crystallizes in the orthorhombic space group Pnam with a = 16.465 Å, b = 13.577 Å. c = 7. 621 Å and four molecules per unit cell. The structure has been solved by direct methods and refined to a final R value of 0.050. The CPPOB molecules have exact C_s symmetry as a consequence of their location on crystallographic mirror symmetry planes, the benzene ring to which the cyano group is attached has a perpendicular orientation to the other ring in the plane. The molecules adopt a nearly optimal stretched form, neighbouring molecules make an angle of 35.2°. The results are discussed in relation to the mesomorphic behaviour of CPPOB.

INTRODUCTION

The compound 4′-cyanophenyl-4-n-pentoxybenzoate abbreviated CPPOB in this paper



was first prepared and characterized by Boller and Scherrer.[1] The following phase transitions have been observed (all temperatures in °C)

$$\begin{tikzcd}
Cr \arrow[rr, "85\text{-}85.5"] & & I \arrow[dl, "76.5\text{-}77"] \\
& N \arrow[ul] &
\end{tikzcd}$$

Therefore, CPPOB forms only a monotropic nematic mesophase but its higher homologues exhibit a reversible transition from crystalline into liquid crystalline state. Because of their electro-optical behaviour and other appropriate properties the substituted cyanophenylbenzoates are of interest as components of materials for liquid crystal displays. For the appearance of one or more liquid crystalline phases some requirements with regard to the chemical constitution as well as to the extent of molecular interactions must be fulfilled. Since the discovery of liquid crystallinity by Reinitzer in 1888 a great number of useful rules concerning the chemical aspects of this problem have been stated. But so far much less is known about the relationships between molecular packing in the solid and the possible occurrence of thermal mesomorphism after melting. The first attempts to correlate the presumed molecular arrangement in the mesophase with the crystal structure of the mesogenic material were undertaken by Bernal and Crowfoot[2] in the early 1930s. Up to now, in all about forty crystal structures determined by X-ray methods have been reported for mesogenic substances, most of them for nematogens. Recently, a preliminary survey of the present knowledge with respect to the solid-mesophase relationships was given by Bryan.[3] According to the above transition scheme the crystalline modification of CPPOB is not a precursor (in the strict meaning of the word) of the nematic phase of this compound. It should be emphasized that neither microscopic, nor calorimetric, nor X-ray studies give any indication of the existence of other crystalline polymorphs.

In the following the crystal structure determination of CPPOB is reported. It has been performed to estimate the exact molecular packing in the solid state and, as a result of that, to make a contribution to the above mentioned problems.

EXPERIMENTAL

Suitable colourless needle-shaped crystals of CPPOB were obtained by recrystallization from ethanol. Weissenberg and de Joung–Bouman photographs indicated orthorhombic symmetry and gave preliminary unit cell parameters. Systematic absences of the reflections (h01) for *h* odd and

(0k1) for $k + l$ odd correspond to those for space groups $Pna2_1$ or Pnam. The density measured by the flotation method using a mixture of ethanol and glycerin indicated four molecules in the unit cell.

The accurate cell dimensions were determined by a least-squares treatment of the angular coordinates of 15 counter reflections. Their values are given in Table I along with other relevant crystal data.

TABLE I

Crystal data

4′-Cyanophenyl-4-n-pentoxybenzoate (CPPOB)
$C_{19}H_{19}NO_3$ M.W. = 309.4
M.p. = 85°C
Orthorhombic
Space group Pnam
$a = 16.465(1)$ Å
$b = 13.577(3)$ Å
$c = 7.621(1)$ Å
$V = 1703.8$ Å^3
$Z = 4$
$D_c = 1.21\ \mathrm{g \cdot cm^{-3}}$ $D_m = 1.15(3)\ \mathrm{g \cdot cm^{-3}}$
$F(000) = 656$
$\mu(\mathrm{CuK}\alpha) = 6.7\ \mathrm{cm^{-1}}$

Three-dimensional intensity data were measured on a Syntex $P2_1$ four-circle diffractometer using graphite-monochromatized CuKα radiation and a crystal with approximate size 0.3 × 0.3 × 0.3 mm^3. Intensities were collected in a 2θ range up to 115° ($\sin\theta/\lambda \leq 0.55$ Å^{-1}) using the θ–2θ scanning mode. For each reflection only the profile was measured, the stationary background measurements being neglected. The background level as well as I and σ(I) for each reflection were then calculated according to the algorithm of Lehmann and Larsen[4] using the computer program PRAN.[5] Of the 1203 measured independent reflections, 970 with $I \geq 1.96\sigma(I)$ were considered observed and used in the structure analysis.

The conversion of intensities into structure factors was performed in the usual way. No absorption or extinction corrections were applied.

STRUCTURE DETERMINATION AND REFINEMENT

The phase problem was solved by direct methods using the computer program MULTAN.[6] Based on the known structures of other phenyl benzoates[7,8] the symmetry of the CPPOB molecule could be expected to be not higher than C_1. Considering the unit cell contents of only four molecules and the symmetry requirements of the general and special positions in the two possible space groups ($Pna2_1$ and Pnam) an assumption was made that the correct space group was that of lower symmetry ($Pna2_1$). MULTAN was therefore run in $Pna2_1$ although the E-value statistics strongly indicated the centrosymmetric space group. After the first unsuccessful run a second attempt was made with the three strongest reflections (2 11 2), (1 12 0) and (11 5 0) rejected and it finally led to the correct solution. The successful MULTAN run was based on 159 reflections with $E \geq 1.45$ and with the origin fixed by (1 11 1), (7 12 0) and (10 6 1) reflections and the multisolution phases assigned to reflections (0 0 4), (1 12 2), (2 11 0) and (3 1 0). Of the 64 generated phase sets that with the best figures of merit (ABS FOM = 1.1781, $R_{\mathrm{Karle}} = 26.50$) was used to calculate an E-map. It revealed the positions of all 23 non-hydrogen atoms ($R = 0.34$). As a pecularity of the E-map, 19 of its potential atomic positions were located in one plane with almost exactly the same z-coordinates and the remaining 4 peaks in two equidistant pairs above and below this plane. This specific atomic arrangement indicated a mirror plane and C_s symmetry of the CPPOB molecule and, as a consequence, Pnam rather than $Pna2_1$ as the correct space group. The space group was then changed to Pnam and the subsequent successful refinements proved this to be correct.

Full-matrix least-squares refinement of the heavy atom structure model yielded after four cycles with isotropic temperature factors an R value of 0.180, and the subsequent four cycles with anisotropic factors reduced R to 0.118. A difference Fourier map calculated at this stage showed well defined electron density peaks at locations that agreed well with the expected positions of all hydrogen atoms. Each hydrogen atom was given an isotropic thermal parameter one unit greater than the isotropic value for the carbon atom to which it was attached. In the further refinement the hydrogen parameters were included in the model for structure factor calculations but they themselves were not refined.

The function minimized in the least-squares refinement was

$$\sum w(|F_0| - |F_c|)^2$$

with w based initially on counting statistics ($w = \sigma^{-2}$). At this stage, however, the initial weighting scheme was replaced with one defined as follows

$$w = (|F_0|/F_{\mathrm{low}})^2 \text{ for } |F_0| < F_{\mathrm{low}}$$

$$w = 1 \text{ for } F_{\mathrm{low}} \leq |F_0| \leq F_{\mathrm{high}}$$

$$w = (F_{\mathrm{high}}/|F_0|)^2 \text{ for } |F_0| > F_{\mathrm{high}}$$

with $F_{\mathrm{low}} = 2.2$ and $F_{\mathrm{high}} = 16$.

Using this weighting scheme two cycles of full-matrix least-squares refinement of all non-hydrogen positional and thermal parameters converged to $R = 0.050$ and $R_w = [\sum w(|F_0| - |F_c|)^2/\sum w|F_0|^2]^{0.5} = 0.058$. These values were accepted as final. The number of observations per parameter varied was 7.3. All calculations were performed using the SYNTEX XTL structure determination programs[9] in the modified version developed at the University of Poznań.[5] Final atomic parameters are listed in Table II, the labelling of

TABLE II

a) Final fractional atomic coordinates × 10^4 and anisotropic temperature factors of non-hydrogen atoms. The anisotropic temperature factors are of the form $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. Estimated standard deviations for last decimal digit are given in parentheses. The labelling of atoms is as shown in Figure 1

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	3089(3)	3127(3)	2500	6.5(2)	4.3(2)	11.0(3)	−0.8(2)	0.0	0.0
C(2)	3411(3)	2081(3)	2500	5.5(2)	4.5(2)	9.1(3)	−0.5(2)	0.0	0.0
C(3)	2750(2)	1320(2)	2500	5.8(2)	4.1(2)	5.3(2)	−0.5(1)	0.0	0.0
C(4)	3078(2)	268(3)	2500	5.4(2)	4.0(2)	6.8(2)	−0.3(1)	0.0	0.0
C(5)	2402(2)	−473(3)	2500	5.8(2)	3.9(2)	7.3(3)	−0.3(1)	0.0	0.0
C(6)	2253(2)	−2238(2)	2500	5.6(2)	3.8(2)	4.9(2)	−0.6(2)	0.0	0.0
C(7)	1419(2)	−2185(3)	2500	5.2(2)	3.9(2)	8.3(3)	0.2(2)	0.0	0.0
C(8)	2632(2)	−3148(3)	2500	5.0(2)	4.2(2)	6.1(2)	−0.1(1)	0.0	0.0
C(9)	2181(2)	−3999(2)	2500	4.9(2)	3.8(2)	5.9(2)	−0.0(1)	0.0	0.0
C(10)	1340(2)	−3957(2)	2500	5.5(2)	3.5(2)	5.4(2)	−0.6(1)	0.0	0.0
C(11)	966(2)	−3042(3)	2500	4.8(2)	4.5(2)	8.8(3)	−0.2(2)	0.0	0.0
C(12)	828(3)	−4842(3)	2500	5.1(2)	4.4(2)	7.3(3)	−0.2(2)	0.0	0.0
C(13)	910(2)	−6593(3)	2500	5.1(2)	3.9(2)	7.1(3)	−0.5(1)	0.0	0.0
C(14)	770(2)	−7048(2)	4058(4)	7.8(2)	5.3(1)	6.2(2)	−1.6(1)	0.4(1)	−0.8(1)
C(15)	493(2)	−8011(2)	4061(4)	7.4(2)	5.0(1)	6.4(2)	−1.3(1)	0.6(1)	0.3(1)
C(16)	356(2)	−8486(2)	2500	5.0(2)	3.4(2)	6.9(2)	−0.5(1)	0.0	0.0
C(17)	69(3)	−9492(3)	2500	6.8(2)	4.4(2)	7.1(3)	0.2(2)	0.0	0.0
O(1)	2762(2)	−1439(2)	2500	5.4(1)	3.6(1)	8.0(2)	−0.5(1)	0.0	0.0
O(2)	108(2)	−4870(2)	2500	5.2(2)	5.4(2)	19.1(4)	−0.5(1)	0.0	0.0
O(3)	1284(2)	−5670(2)	2500	5.0(1)	3.8(1)	9.9(2)	−1.0(1)	0.0	0.0
N(1)	−153(3)	−287(3)	2500	10.3(3)	3.9(2)	8.7(3)	−1.0(2)	0.0	0.0

b) Fractional coordinates × 10^3 and isotropic temperature factors (Å^2) of hydrogen atoms used in the least-squares calculations. The numbers are those of the carbon atoms to which the hydrogens are attached

Atom	x/a	y/b	z/c	B_{iso}	Atom	x/a	y/b	z/c	B_{iso}
H(1A)	346	363	250	7.4	H(7)	114	−152	250	6.3
H(1B)	272	327	347	7.4	H(8)	322	−321	250	5.7
H(2)	382	197	345	6.8	H(9)	244	−466	250	5.3
H(3)	236	142	352	5.7	H(11)	38	−303	250	6.2
H(4)	349	13	345	6.2	H(14)	86	−677	515	6.8
H(5)	202	−39	152	5.9	H(15)	36	−834	516	6.7

atoms is shown in Figure 1. A list of observed and calculated structure factors is available from the authors on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Molecular structure

The molecular geometry is shown in Figure 1. The potential molecular symmetry of CPPOB is fully developed in the structure, the molecule exhibits exact C_s symmetry required by its location on the crystallographic mirror plane. The cyanophenyl group is perpendicular to the mirror plane whereas the other phenyl ring and the —C(O)O— group are coplanar and located in the mirror plane.

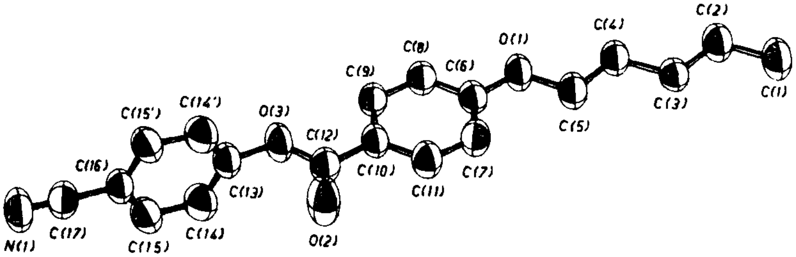


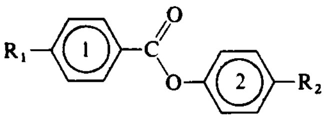
FIGURE 1 Molecular structure of CPPOB (drawn by use of ORTEP) showing the atomic numbering system.

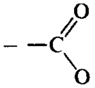
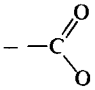
The molecular conformation established for CPPOB in this work is quite surprising when compared with other similar systems. As far as we know, at present no other crystal structures of phenyl benzoates are known than those reported for the unsubstituted compound itself (PB)[7] and for 4'-nitrophenyl-4-*n*-octoxybenzoate (NPOOB).[8] Table III presents a compilation of molecular geometry data for the three compounds in question. Both PB and NPOOB have only C_1 symmetry and the deviation from C_s symmetry is very significant. Particularly remarkable is the difference between NPOOB and CPPOB regarding the conformation about the C(10)–C(12) bond since from the chemical point of view the substituents at the benzene rings in these compounds are rather similar. There is no simple explanation for the differences in the stereochemical behaviour of the phenyl benzoates unless they can be accounted for by the effects of crystal packing. The bond distances and angles are given in Table IV, the numbering of the atoms is indicated in Figure 1.

All values are similar to the usual values and in particular show a good agreement with those in PB and NPOOB (Table III). Therefore only a few details of molecular dimensions will be discussed here.

TABLE III

Relevant parameters of molecular structure for crystalline phenyl benzoates



	PB[a] $R_1 = H$ $R_2 = H$	NPOOB[b] OC_8H_{17} NO_2	CPPOB OC_5H_{11} CN
Bond lengths (Å)			
C—O	1.371(6)	1.36(1)	1.352(4)
C=O	1.194(6)	1.20(1)	1.186(5)
C—C (ring 1)	1.487(6)	1.47(1)	1.467(5)
O—C (ring 2)	1.413(5)	1.41(1)	1.395(4)
Bond angles (°)			
O=C—O	123.1(4)	123.2(7)	121.8(3)
O=C—C (ring 1)	126.0(4)	125.2(6)	126.9(3)
O—C—C (ring 1)	110.9(4)	111.6(5)	111.3(3)
C—O—C (ring 2)	118.3(4)	118.7(5)	120.1(2)
Dihedral angles (°)			
Ring 1 — 	65.1	1.98	0
Ring 2 — 	−9.8	58.14	90

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[a] PB = phenyl benzoate, v. Ref. 7.

[b] NPOOB = 4′-nitrophenyl-4-n-octoxybenzoate, v. Ref. 8.

The average bond lengths (Å) and angles (°) for the benzene rings are

		C—C	C—C—C
Ring 1	C(6)...C(11)	1.381(5)*	120.0(7)*
Ring 2	C(13)...C(16)	1.372(10)*	120.3(1.0)*

(* Standard deviation of individual values from the average)

They do not differ significantly from each other and from the expected values of respectively 1.395 Å[10] and 120.0°. Except for the relatively short C(13)-C(14) bond also the range of individual bond lengths (Table IV) is within experimental error. The mean value for the alkyl C—C bond length

TABLE IV

Bond distances and angles for the non-hydrogen atoms (esd's in parentheses)

Atoms	Distance (Å)	Atoms	Angle (°)
Carboxylic group			
C(12)—O(2)	1.186(5)	O(2)—C(12)—O(3)	121.8(3)
C(12)—O(3)	1.352(4)	O(2)—C(12)—C(10)	126.9(3)
C(12)—C(10)	1.467(5)	O(3)—C(12)—C(10)	111.3(3)
O(3)—C(13)	1.395(4)	C(12)—O(3)—C(13)	120.1(2)
Benzene ring 1			
C(6)—C(8)	1.384(5)	C(7)—C(6)—C(8)	119.8(3)
C(8)—C(9)	1.373(5)	C(6)—C(8)—C(9)	120.5(3)
C(9)—C(10)	1.386(5)	C(8)—C(9)—C(10)	120.4(3)
C(10)—C(11)	1.386(5)	C(9)—C(10)—C(11)	118.7(3)
C(11)—C(7)	1.382(5)	C(10)—C(11)—C(7)	121.0(3)
C(7)—C(6)	1.375(6)	C(11)—C(7)—C(6)	119.7(3)
		O(1)—C(6)—C(7)	124.7(3)
		O(1)—C(6)—C(8)	115.5(3)
		C(12)—C(10)—C(9)	122.7(3)
		C(12)—C(10)—C(11)	118.6(3)
Benzene ring 2			
C(13)—C(14)	1.359(4)	C(14)—C(13)—C(14′)	121.9(3)
C(14)—C(15)	1.384(4)	C(13)—C(14)—C(15)	119.2(3)
C(15)—C(16)	1.372(4)	C(14)—C(15)—C(16)	119.8(3)
		C(15)—C(16)—C(15′)	120.2(3)
		O(3)—C(13)—C(14)	118.9(3)
		C(15)—C(16)—C(17)	119.9(3)
Alkoxy group			
C(1)—C(2)	1.516(5)	C(1)—C(2)—C(3)	113.0(3)
C(2)—C(3)	1.501(5)	C(2)—C(3)—C(4)	112.7(3)
C(3)—C(4)	1.528(5)	C(3)—C(4)—C(5)	111.3(2)
C(4)—C(5)	1.500(5)	C(4)—C(5)—O(1)	107.8(2)
C(5)—O(1)	1.440(4)	C(5)—O(1)—C(6)	118.1(2)
O(1)—C(6)	1.370(4)		
Cyano group			
N(1)—C(17)	1.140(5)	N(1)—C(17)—C(16)	179.7(4)
C(16)—C(17)	1.445(5)		

is 1.511(12) Å, i.e. a bit less than the standard value of 1.541 Å for paraffines,[10] but such a slight shortening is a common phenomenon. Also the slight enlargening of the C—C—C angles (average 112.3(7)°) is quite normal.

The C—H distances range from 0.92 to 1.02 Å with a mean value of 0.98 Å.

Molecular packing

Figure 2 shows the packing arrangement of CPPOB molecules in the crystal projected down the *c*-axis. For the sake of clear presentation of the geometric relations a scheme of symmetry elements in the space group Pnam is incorporated in Figure 2.

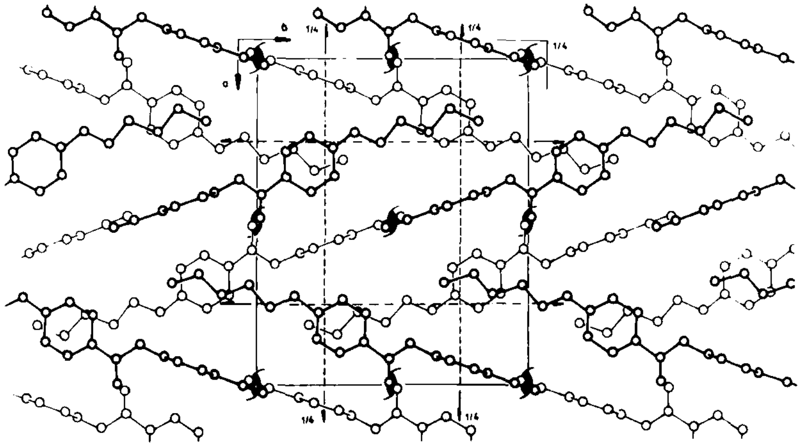

FIGURE 2 Crystal structure of CPPOB projected down the *c* axis.

All the molecules are located in the mirror planes parallel to *a* and *b* with $z = 1/4$ and 3/4. The molecular axis (line connecting the two benzene ring centers) makes an angle of 17.6° with the *y*-axis. By translation along *a* and *b* and by the action of the space group *a*-glide plane, sheets of molecules are formed. The benzene ring C(6)...C(11) is parallel to the sheet surface whereas the other benzene ring C(13)...C(16) is perpendicular to it. The interaxial angle of neighbouring molecules is 35.2°. In this way a herringbone packing of molecules within the sheets is generated. The sheets on their part are stacked atop one another by the action of the space group *c*-glide. The vertical displacement within the stack is $c/2 = 3.8$ Å.

No remarkable imbrication of the molecules in the crystal structure of CPPOB is observed either within the sheets or within the stacks.

In the introduction to this paper a reference has been made to the mesomorphic behaviour of CPPOB. The fact that this compound fails to form a nematic phase on heating can be roughly explained by the characteristic features of its crystal structure. Many authors believe[3] that a parallel imbricated mode of molecular packing in the crystalline phase contiguous to the melt is a necessary condition for a compound to form a nematic liquid crystal. This prerequisite is, however, not fulfilled in the crystal structure of CPPOB, as described above. The structure exhibits neither a general parallelism nor a sufficient imbrication of the molecules, and under these unfavourable conditions there is obviously no spontaneous tendency to develop a parallel alignment as the solid breaks down. Still, it should be emphasized that CPPOB according to its molecular properties is a real nematogenic compound. Its ability to form a mesophase has been proved by experimental work: By slow cooling CPPOB forms a monotropic nematic phase in a wide range of more than forty degrees below the melting point.

The problem of molecular packing in organic crystals was discussed in detail by Kitaigorodski.[11] In particular he called a special attention to the general validity of close-packing principle for organic molecules in the crystalline state. The packing coefficients for the overwhelming majority of known crystal structures are between 0.65–0.77. It has been proved[11] that molecules with a mirror symmetry plane and retaining this symmetry element in the crystal can be packed with maximum density only in the space groups $Pmc2_1$, $Cmc2_1$ and Pnma. Among these the most frequently encountered for crystal structures is Pnma. Our results obtained for CPPOB agree well with these principles: The confirmed space group is Pnam and the packing coefficient has been estimated to 0.71. For calculating the molecular volume (304.1 Å^3) the volume increments given by Immirci and Perini[12] have been used.

TABLE V

Intermolecular contacts in the crystal structure of CPPOB

From atom in x, y, z	To atom	In position	Distance (in Å)
N(1)	C(7)	$x, 1 + y, z$	3.652(5)
N(1)	C(15)	$-x, -1 - y, 1/2 + z$	3.539(4)
N(1)	C(17)	$-x, -1 - y, -1/2 + z$	3.825(5)
N(1)	N(1)	$-x, -1 - y, -1/2 + z$	3.922(4)
C(1)	C(13)	$x, 1 + y, z$	3.608(6)
C(1)	O(3)	$x, -1 + y, z$	3.391(6)
C(14)	O(1)	$1/2 - x, 1/2 + y, -1/2 + z$	3.662(4)
C(4)	O(2)	$1/2 + x, -1/2 - y, z$	3.386(5)

Table V lists the most relevant intermolecular non-hydrogen atomic distances in the structure. They are without exception greater than the sums of the appropriate van der Waals radii. Also the shortest N...H, O...H, C...H and H...H distances are consistent with the normal van der Waals-type contacts. Judging from the actual nonbonded contacts between the cyano groups of molecules related by the 2_1 axis (see N(1)...C(17) and N(1)...N(1) in Table V) there is no remarkable influence of opposed dipoles on the crystal packing.

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