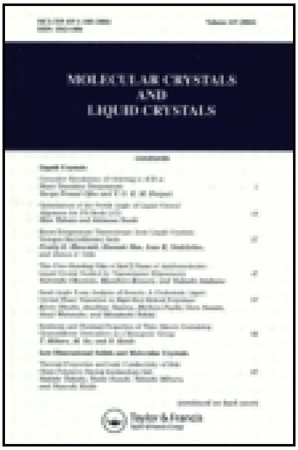

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The Crystal and Molecular Structure of 4'-Cyanophenyl-4-n-Pentylbenzoate

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The Crystal and Molecular Structure of 4′-Cyanophenyl-4-*n*-Pentylbenzoate

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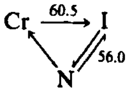
The crystal and molecular structure of the title compound with the formula C_5H_{11}—C_6H_4—COO—C_6H_4—CN (CPPB) has been determined by X-ray diffraction methods. CPPB crystallizes in the monoclinic space group $P2_1/n$ with eight molecules in a unit cell of dimensions a = 15.268(2) Å, b = 9.165(1) Å, c = 24.031(3) Å, β = 94.67(1)°. The structure has been solved by direct methods and refined to an R value of 0.070.

The CPPB molecules adopt a stretched form and are packed in an approximate parallel imbricated mode, the molecular long axes making an angle of about 5° with the crystal c axis. The molecular geometry and packing are discussed in relation to the mesomorphic behavior of CPPB.

INTRODUCTION

As part of a series of X-ray structural investigations on mesogenic compounds in their crystalline state we reported recently in this journal[1] the structure of 4′-cyanophenyl-4-*n*-pentoxybenzoate (CPPOB). In this paper we present the results of an X-ray analysis of the closely related compound 4′-cyanophenyl-4-*n*-pentylbenzoate, C_5H_{11}—C_6H_4—COO—C_6H_4—CN (hereafter CPPB).

In contrast to its higher homologues exhibiting reversible transitions from crystalline into liquid crystalline state, CPPB forms only a monotropic nematic phase. Boller and Scherrer[2] observed the following phase transitions (temperature in °C)



This thermal behavior is analogous to that of CPPOB. As stated in our earlier paper,[1] the principal aim of our structural studies in the field of crystalline mesogenic compounds is to obtain molecular packing schemes in the solid as a starting point for a discussion of the solid-mesophase relationships. Equally interesting is the question of how the mesomorphic behavior of a compound is influenced by the substituent-affected conformation of its molecules. This aspect is of particular interest in the case of CPPB because for the closely similar compound, CPPOB, unexpectedly high molecular symmetry, C_s, was found,[1] a feature unique in the class of phenyl benzoates.

Experimental

CPPB crystallizes from ethanol in the form of colorless needles. Diffraction patterns indicated monoclinic symmetry and gave preliminary lattice parameters. The space group $P2_1/n$ was uniquely determined from the observed systematic absences of reflections $h0l$ with $h + l = 2n + 1$ and $0k0$ with $k = 2n + 1$. Precise unit cell dimensions were de-

TABLE I

Crystal data	
4′-Cyanophenyl-4-*n*-pentylbenzoate (CPPB)	
$C_{19}H_{19}NO_2$	M.W. = 293.4
M.p. = 60.5°C	
Monoclinic	
Space group $P2_1/n$	
$a = 15.268(2)$ Å	
$b = 9.165(1)$ Å	
$c = 24.031(3)$ Å	
$\beta = 94.67(1)$ °	
$V = 3351.5$ Å^3	
$Z = 8$	
$D_c = 1.16$ g·cm^{-3}	$D_m = 1.13(3)$ g·cm^{-3}
F(000) = 1248	
$\mu(\text{CuK}_\alpha) = 5.2$ cm^{-1}	

rived from a least-squares treatment of the angular coordinates of 15 counter reflections. Relevant crystal data of CPPB are summarized in Table I.

Intensity data were measured from a crystal with dimensions $0.25 \times 0.32 \times 0.36$ mm^3 mounted on a Syntex P2$_1$ four circle diffractometer in a way described earlier.[1] A total of 4124 independent reflections were measured; of these 2206 had $I \geqslant 1.996 \cdot \sigma(I)$ and were considered as observed and used in the structure analysis. Intensities were reduced to structure factors in the usual way. No correction was made for absorption [$\mu(\mathrm{CuK}_\alpha) = 5.2$ cm^{-1}].

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The structure was solved by means of the centrosymmetric direct methods program EEES included in the SHELX-76 system.[3] Nineteen hundred and ninety-nine Σ_2-relationships were generated for the reflections with $|E| \geqslant 1.2$. The starting set consisted of the three origin fixing and fourteen other reflections. The sixth of the ten E-maps computed showed chemically reasonable models of the two symmetry-independent molecules and revealed the positions for 41 of the 44 heavy atoms. The three remaining atoms were located in a Fourier map.

Full-matrix least-squares refinement of the non-hydrogen atoms with isotropic temperature factors resulted in an R-value of 0.154. After anisotropic refinement of these atoms (to R = 0.119) the H atoms were located in a difference Fourier map. Each H atom was given an isotropic thermal parameter equal to the isotropic value for the carbon atom to which it was attached. Subsequent anisotropic refinement in which the parameters of the H atoms were kept fixed converged at R = 0.087. This relatively high R-value is probably due to the effects of structural disorder and to extinction. The thermal parameters of the alkyl chain atoms in molecule I have irregularly high values (as compared with those in molecule II). In addition the positional parameters of the corresponding H atoms located by the difference Fourier synthesis did not meet the expectation. Therefore all H atoms of the alkyl chain of molecule I and the H atoms at C(II1) of molecule II were placed in calculated positions (C—H = 1.08 Å, tetrahedral coordination of C atoms) and these coordinates were used in the final refinement. Moreover, eight strong reflections with large $\Delta F/\sigma(F)$ were excluded from the refinement. This reduced R to 0.070 which was accepted as final.

TABLE II

a) *Final fractional atomic coordinates* ($\times 10^4$) with estimated standard deviations in parentheses and isotropic equivalents ($\times 10^3$) of the anisotropic thermal parameters for the non-hydrogen atoms
$U_{eq} = 1/3\,(U_{11} + U_{22} + U_{33} + 2\,U_{13}\cos\beta)$

	Molecule I				Molecule II			
Atom	*x/a*	*y/b*	*z/c*	U_{eq}(Å^2)	*x/a*	*y/b*	*z/c*	U_{eq}(Å^2)
C(1)	9095(6)	3026(11)	2761(4)	147	5931(4)	4638(8)	7299(2)	97
C(2)	9022(5)	3689(10)	3316(4)	124	5948(4)	3865(7)	6748(3)	90
C(3)	9006(6)	2587(10)	3761(3)	140	6080(4)	4874(7)	6264(2)	73
C(4)	8884(6)	3279(10)	4328(4)	147	6120(4)	4129(7)	5696(2)	72
C(5)	8646(5)	2266(8)	4767(2)	94	6244(4)	5247(7)	5244(2)	73
C(6)	8603(4)	2867(8)	5347(2)	76	6302(4)	4670(7)	4658(2)	68
C(7)	8675(4)	4342(7)	5472(2)	79	6410(4)	5648(7)	4223(3)	76
C(8)	8648(4)	4846(7)	6014(2)	78	6470(4)	5147(7)	3680(2)	72
C(9)	8539(4)	3869(7)	6443(2)	68	6397(4)	3673(7)	3561(2)	66
C(10)	8447(4)	2393(7)	6326(3)	77	6285(4)	2702(6)	3991(3)	77
C(11)	8475(4)	1907(7)	5782(3)	78	6242(4)	3201(7)	4529(2)	77
C(12)	8531(4)	4478(8)	7012(3)	75	6423(4)	3067(8)	2988(3)	73
C(13)	8582(5)	3782(7)	7976(3)	77	6522(4)	3760(7)	2042(2)	72
C(14)	9329(4)	4406(8)	8233(3)	89	7244(4)	4188(7)	1776(3)	75
C(15)	9364(4)	4628(8)	8807(3)	88	7251(4)	3944(7)	1207(3)	79
C(16)	8667(4)	4244(7)	9099(2)	74	6527(5)	3292(7)	923(2)	75
C(17)	7923(4)	3630(7)	8831(2)	77	5808(4)	2845(8)	1199(3)	92
C(18)	7885(4)	3398(7)	8259(3)	78	5802(4)	3100(8)	1763(3)	89
C(19)	8721(4)	4416(7)	9702(3)	82	6510(5)	3090(8)	319(3)	92
N(1)	8772(4)	4507(7)	10177(2)	106	6489(4)	2957(7)	−152(3)	123
O(1)	8522(3)	5736(5)	7143(2)	101	6355(3)	1815(5)	2866(2)	94
O(2)	8560(3)	3399(5)	7405(2)	88	6530(3)	4150(4)	2609(2)	84

TABLE II

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

	Molecule I				Molecule II			
Atom	x/a	y/b	z/c	U_{iso}(Å^2)	x/a	y/b	z/c	U_{iso}(Å^2)
H(1a)	918	390	247	130	539	541	729	86
H(1b)	858	237	266	130	655	522	736	86
H(1c)	973	239	279	130	588	387	764	86
H(2a)	846	437	325	110	637	319	675	75
H(2b)	961	436	339	110	557	307	667	75
H(3a)	847	193	368	128	667	534	636	65
H(3b)	961	187	384	128	554	566	620	65
H(4a)	840	407	440	123	554	361	562	68
H(4b)	954	375	443	123	664	337	570	68
H(5a)	815	148	462	87	571	602	525	64
H(5b)	928	187	469	87	688	589	530	64
H(7)	880	505	514	71	683	673	428	68
H(8)	868	599	612	67	672	583	338	66
H(10)	831	160	665	69	627	157	386	70
H(11)	839	80	566	67	615	247	485	70
H(14)	985	502	801	78	780	479	195	64
H(15)	988	547	902	76	780	427	99	71
H(17)	732	319	905	66	536	213	100	79
H(18)	736	284	804	65	528	270	196	74

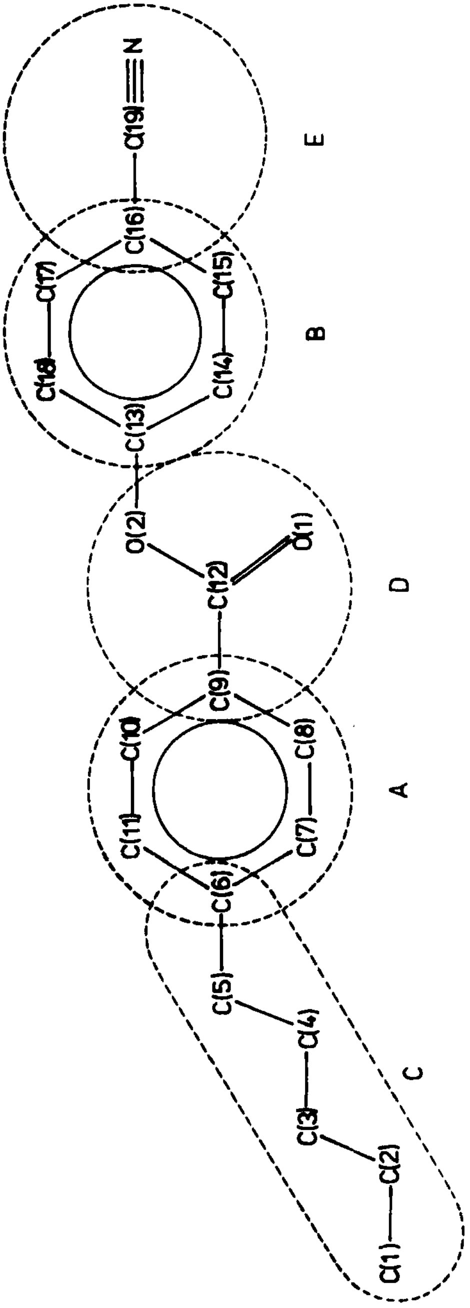


FIGURE 1 Atom-numbering scheme in molecules of CPPB

Throughout the refinement unit weights were used. All computations were performed with the SHELX-76 system on an ESER-1040 computer of the Halle University.

Final values of the atomic parameters are given with their standard deviations in Table II. Atomic labelling scheme is that employed in Figure 1. In the following discussion the two independent molecules are referred to as molecule I and II.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Molecular structure

A stereoscopic ORTEP drawing of the two independent molecules is given in Figure 2. As can be seen, both molecules adopt a widely stretched and nearly linear form, so that the general geometric condition required for molecules forming liquid crystals is fulfilled by CPPB.

The bond distances and angles are tabulated in Table III. For the cyanophenyl benzoate part, the corresponding values of both mole-

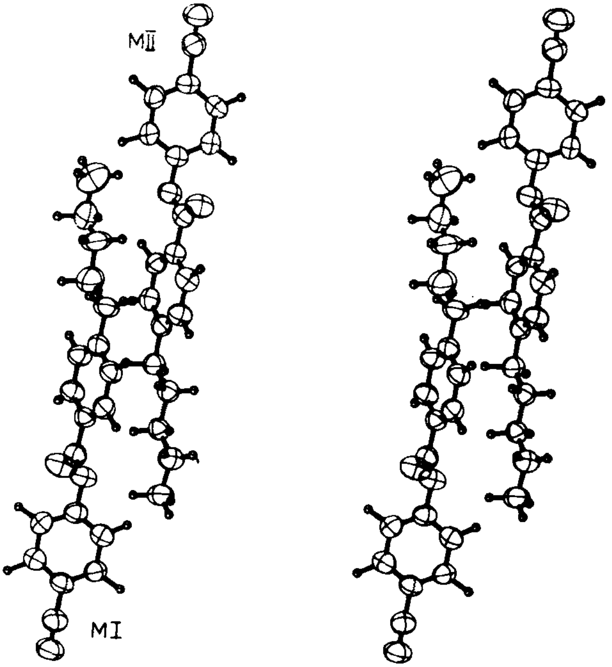


FIGURE 2 Stereoscopic ORTEP drawing of the two independent CPPB molecules MI and MII

TABLE III

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

	Distance (Å)			Angle (°)	
Atoms	Molecule I	Molecule II	Atoms	Molecule I	Molecule II
			Benzene ring A		
C(6)—C(7)	1.387(10)	1.397(9)	C(6)—C(7)—C(8)	121.3(6)	120.7(6)
C(7)—C(8)	1.388(8)	1.393(9)	C(7)—C(8)—C(9)	119.9(6)	120.3(6)
C(8)—C(9)	1.386(9)	1.383(9)	C(8)—C(9)—C(10)	119.7(5)	119.2(5)
C(9)—C(10)	1.386(9)	1.383(9)	C(9)—C(10)—C(11)	119.7(6)	120.3(6)
C(10)—C(11)	1.385(9)	1.379(9)	C(10)—C(11)—C(6)	121.4(6)	121.7(6)
C(11)—C(6)	1.392(9)	1.383(9)	C(11)—C(6)—C(7)	117.9(6)	117.8(5)
			C(5)—C(6)—C(7)	123.2(6)	119.5(6)
			C(5)—C(6)—C(11)	118.9(6)	122.7(5)
			C(8)—C(9)—C(12)	117.1(6)	123.2(6)
			C(10)—C(9)—C(12)	123.2(6)	117.7(6)
			Benzene ring B		
C(13)—C(14)	1.377(9)	1.375(9)	C(13)—C(14)—C(15)	118.0(6)	118.9(5)
C(14)—C(15)	1.390(9)	1.385(9)	C(14)—C(15)—C(16)	120.2(6)	119.1(6)
C(15)—C(16)	1.367(10)	1.386(9)	C(15)—C(16)—C(17)	120.7(6)	121.4(6)

C(16)—C(17)	1.379(9)	1.391(10)	C(16)—C(17)—C(18)	119.5(6)	119.3(6)
C(17)—C(18)	1.387(9)	1.375(9)	C(17)—C(18)—C(13)	119.1(6)	118.9(6)
C(18)—C(13)	1.354(10)	1.380(9)	C(18)—C(13)—C(14)	122.6(6)	122.4(6)
			O(2)—C(13)—C(14)	119.5(6)	115.7(5)
			O(2)—C(13)—C(18)	117.7(6)	121.6(6)
			C(15)—C(16)—C(19)	120.0(6)	119.6(6)
			C(17)—C(16)—C(19)	119.2(6)	119.1(6)
			Pentyl group C		
C(1)—C(2)	1.477(13)	1.503(9)	C(1)—C(2)—C(3)	112.4(8)	113.7(6)
C(2)—C(3)	1.474(13)	1.512(9)	C(2)—C(3)—C(4)	112.0(8)	115.5(5)
C(3)—C(4)	1.528(12)	1.533(8)	C(3)—C(4)—C(5)	115.6(8)	110.7(5)
C(4)—C(5)	1.473(11)	1.516(8)	C(4)—C(5)—C(6)	117.7(6)	116.8(5)
C(5)—C(6)	1.505(9)	1.513(8)			
			Carboxylic group D		
C(9)—C(12)	1.478(9)	1.490(9)	C(9)—C(12)—O(1)	127.5(6)	125.5(6)
C(12)—O(1)	1.196(9)	1.186(9)	C(9)—C(12)—O(2)	111.4(6)	111.0(6)
C(12)—O(2)	1.365(8)	1.365(8)	O(1)—C(12)—O(2)	121.1(6)	123.5(6)
O(2)—C(13)	1.414(7)	1.410(7)	C(12)—O(2)—C(13)	119.2(5)	118.0(5)
			Cyano group E		
C(16)—C(19)	1.454(9)	1.460(9)	C(16)—C(19)—N	177.9(7)	178.7(8)
C(19)—N	1.140(9)	1.138(10)			

cules are equal within 3σ limit and in good agreement with those reported in literature.

The average C—C bond lengths in the benzene rings are 1.382(3) Å (molecule I) and 1.384(3) Å (molecule II). (Here, as well as in the following, the standard deviations given for mean values represent a scatter of the individual values from the mean). Also the dimensions of the carboxylic and cyano groups are quite normal. The values for the bond distances and angles of the carboxylic group agree well with standard dimensions based on an analysis of appropriate structural data stored in the Cambridge Crystallographic Database.[5] The deviation from linearity for the cyanogroups are similar to those observed for 4′-cyanophenyl-4-*n*-pentylcyclohexanoate (angle C—C—N = 178.7°)[4] and *p*-cyanobenzoic acid (176.4°).[6]

The hydrocarbon chains are strongly influenced by thermal vibrations resulting in a shortening of the average C—C bond lengths [1.491(11) Å for molecule I and 1.515(5) Å for molecule II] and a wid-

TABLE IV

Least squares planes

a) Deviations (Å) of the atoms from the planes A-D defined in Figure 1

Plane	Atoms					
Benzene ring	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)
I A	0.011	−0.006	−0.003	0.007	−0.002	−0.007
II A	0.010	−0.008	0.009	−0.004	−0.003	0.004
	C(13)	C(14)	C(15)	C(16)	C(17)	C(18)
I B	−0.003	0.004	−0.002	−0.001	0.002	0.000
II B	0.001	−0.001	−0.004	0.009	−0.009	0.004
Pentyl Group	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
I C	−0.057	−0.046	0.134	0.073	−0.086	−0.019
II C	0.011	−0.009	−0.005	0.002	−0.008	0.008
Carboxyl group	C(9)	C(12)	O(1)	O(2)		
I D	0.003	−0.009	0.004	0.003		
II D	−0.001	0.002	−0.001	−0.001		

b) Interplanar angles (°)

Planes	Angle	
	Molecule I	Molecule II
A/B	60.0	59.4
A/C	3.6	0.5
A/D	9.1	1.3
B/D	68.2	58.8

ening of the C—C—C bond angles [114(1)° for both molecules] as compared with the standard values. In particular some of the C—C distances of the pentyl group in molecule I are abnormally short.

The geometry of the CPPB molecule is uniquely characterized by conformational relationships of the five structural fragments A–E marked in Figure 1. As seen from Table IV, the phenyl groups are exactly planar. The torsion angle of the bridging carboxylic group C(9)—C(12)—O(2)—C(13) amounts 178.2° (I) and 176.8° (II). Together with the valence angles at C(12) and O (2) (Table III) it is responsible for the parallel orientation of the axes of the benzene rings A and B and for the stretched conformation of the middle part of the molecules.

Interesting conformational features in phenyl benzoates are the interplanar angles between the carboxylic group and the adjacent benzene rings. As stated in our earlier paper,[1] the number of data for comparison in this field is rather limited. For CPPOB the exact C_s symmetry has been found whereas the unsubstituted phenyl benzoate (PB)[7] as well as 4′-nitrophenyl-4-*n*-octoxybenzoate (NPOOB)[8] have only C_1 symmetry, their deviations from C_s symmetry being significant. But the conformation of the two latter compounds is very similar to that found for CPPB. For the sake of clarity and better comparability the relevant values of the four compounds in question are summarized in Table V. (It should be noted here that in the paper on PB[7] the values for the interplanar angles are confused and, unfortunately, this mistake was transferred to our paper about CPPOB.[1]) It can be seen that the three non-symmetric benzoates have rather similar conformations and only CPPOB is an exception. The A/D angle is rather small and in its relatively narrow range the extreme value of 0° for CPPOB could be included. In case of the B/D angle however the 90° value found for that compound is far from the "normal" 58° to 68° range. The reason for that should be due to crystal packing effects.

An overall A/B twist of the two benzene rings in the two independ-

TABLE V

Interplanar angles (°) between the carboxylic group and the benzene rings in crystalline phenyl benzoates (labelling of planes according to Figure 1)

				CPPB	
Planes	PB	NPOOB	CPPOB	Molecule I	Molecule II
A/D	9.8	2.0	0	9.1	1.3
B/D	65.1	58.1	90	68.2	58.8
A/B	55.7	57.1	90	60.0	59.4

ent CPPB molecules is the same (60.0° and 59.4°) but its distribution between the two components A/D and B/D is rather different.

The alkyl chains in both molecules have an all-trans planar extended conformation (nearly ideal for molecule II, but only approximately for molecule I with deviations from the ideal 180° torsion angle up to 14.3°). In molecule II the pentyl group is perfectly and in molecule I nearly co-planar with the adjacent benzene ring (cp. values for the interplanar A/C angle in Table IV).

Molecular packing

The molecular packing in the crystal structure of CPPB is demonstrated in Figure 3 showing a projection in the [010]- direction with the symmetry elements of the space group $P2_1/n$.

The two independent molecules are related by an approximate noncrystallographic center of symmetry at [[0.5, 0.38, 0.25]]. Their long axes connecting the centers of benzene rings A and B make angles of about 5° with the c-axis.

Translation of the two independent molecules along y and z generates sheets parallel to the bc-plane (Figure 4). Neighboring sheets are related by the alternating action of 2_1- axes and inversion centers.

The angle of about 10° between the long axes of molecules I and II leads to a slight tendency to a herringbone arrangement within the sheets, but this angle is too small compared with the herringbone sheets in CPPOB[1] to have any serious influence on the phase behavior of CPPB. Thus, the molecular arrangement should rather be interpreted as an approximate parallel imbricated packing mode, in which the ends of one molecule lie opposite the centers of adjacent molecules. Although with that the geometric prerequisite to give a nematic phase via a displacive transition[9] is fulfilled, CPPB doesn't form a nematic phase on heating but only by undercooling below the melting point, as described in the Introduction. A simple reason for this thermal behavior is that the parallel imbrication of stretched molecules may be taken as a necessary but cannot be taken as a sufficient condition. In addition to the geometric requirements the intermolecular forces play a decisive role in the process of mesophase formation.

All intermolecular contacts between non-hydrogen atoms are greater than the sum of the appropriate van der Waals radii (Table VI).

Acknowledgment

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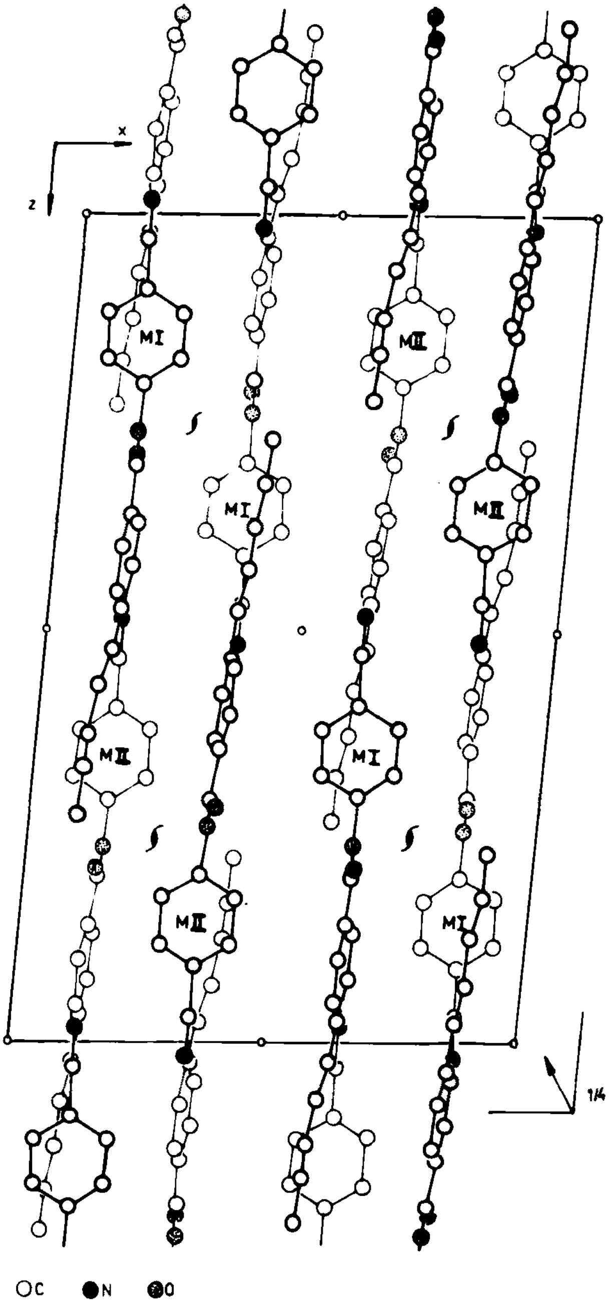

FIGURE 3 Crystal structure of CPPB projected down the b-axis

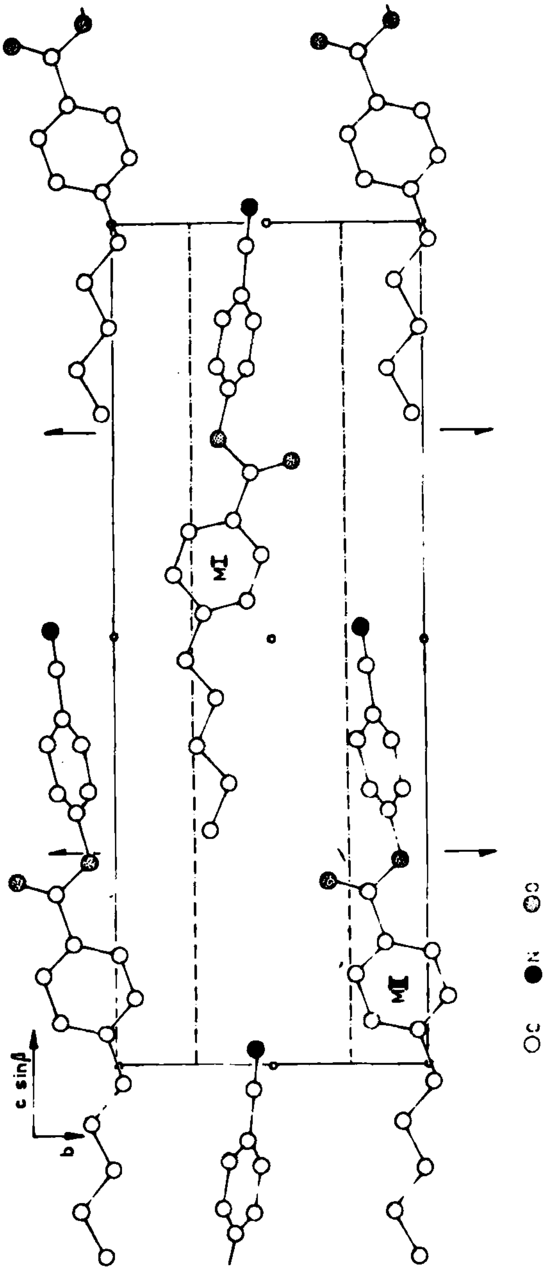

FIGURE 4 A sheet of molecules in the crystal of CPPB formed by the *b*- and *c*-translations.

TABLE VI

Intermolecular contacts shorter than the sum of the appropriate van der Waals radii plus 0.3 Å involving non-hydrogen atoms

From atom to atom		In position			Distance (Å)
C(I1)	C(II14)	*x*	*y*	*z*	3.694
C(I10)	C(II17)	0.5 + *x*	1.5 − *y*	0.5 + *z*	3.648
C(I10)	C(II18)	0.5 + *x*	1.5 − y	0.5 + *z*	3.690
C(I11)	C(II17)	1.5 + *x*	1.5 + *z*	1.5 + *z*	3.628
C(I15)	C(II10)	0.5 + *x*	1.5 − *y*	0.5 + *z*	3.627
C(II11)	N(I)	1.5 − *x*	−0.5 + *y*	1.5 − *z*	3.459
C(I7)	N(II)	1.5 − *x*	0.5 + *y*	0.5 − *z*	3.405
C(I8)	N(II)	1.5 − *x*	−0.5 + *y*	0.5 − *z*	3.520
C(I17)	N(II)	*x*	*y*	−1 + *z*	3.467
C(I18)	O(I1)	1.5 − *x*	0.5 + *y*	1.5 − *z*	3.341
C(I14)	O(II1)	0.5 + *x*	−0.5 − *y*	0.5 + *z*	3.471
C(II14)	O(II1)	1.5 − *x*	−0.5 + *y*	0.5 − *z*	3.289

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