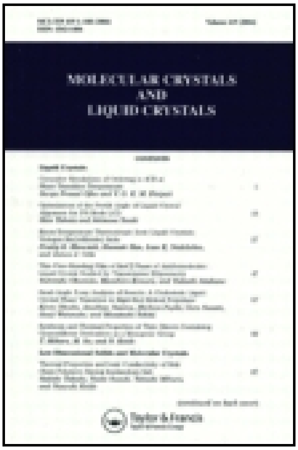

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

An X-ray Study of Cyanophenyl Pyrimidines. Part I-Crystal Structure of PCCPP

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Version of record first published: 04 Oct 2006.

To cite this article: P. Mandal, B. Majumdar, S. Paul, H. Schenk & K. Goubitz (1989): An X-ray Study of Cyanophenyl Pyrimidines. Part I-Crystal Structure of PCCPP, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 168:1, 135-146

To link to this article: http://dx.doi.org/10.1080/00268948908045966

Mol. Cryst. Liq. Cryst., 1989, Vol. 168, pp. 135–146
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Printed in the United States of America

An X-ray Study of Cyanophenyl Pyrimidines. Part I—Crystal Structure of PCCPP

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(*Received April 27, 1988; in final form June 11, 1988*)

The crystal and molecular structures of the nematogen 5-(*trans*-4-ethylcyclohexyl)-2-(4-cyanophenyl)-pyrimidine have been determined by direct methods. The crystal belongs to the monoclinic system with space group *P2/a*, $a = 18.437$, $b = 7.1027$, $c = 15.342$ Å $\beta = 106.07°$ and $Z = 4$. Least squares refinement leads to $R = 0.049$ ($R_w = 0.048$) for 2246 observed reflections. The molecules are in an almost fully extended conformation. Phenyl and pyrimidine rings are highly planar and lie almost in the *ac* plane. The cyclohexane ring is in chair form. Pairs of molecules related by a centre of symmetry are packed into sheets in the *ac* plane and these sheets are stacked along the *b*-axis. The structure is of a common type for a nematogen and the transition to the mesophase is a simple displacive type. The pairing of molecules resulting from the interaction between opposed dipoles of cyano-groups exists in both the crystalline and the nematic state.

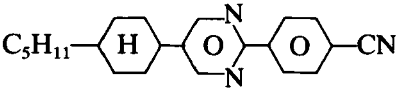
Keywords: X-ray study of a nematogen, crystal structure of a cyanopyrimidine

INTRODUCTION

Mesogenic cyano-compounds are of great interest because of their use in display devices. For a proper understanding of several physical properties of liquid crystal phases a knowledge of the molecular arrangement in the crystalline state is very useful. However, the relationship between the molecular packing in the solid state and the possible occurrence of thermal mesomorphism is yet to be ascertained.[1,2] To study this problem in cyano-compounds we previously determined the crystal and molecular structures of a cyanobiphenyl (50 CB)[3] and a cyanophenyl heptylbenzoate (CPHB).[4] The crystalline modification of 50 CB corresponds to the classical view[5] of a nematogen where the molecules lie in a more or less parallel array and are interleaved in an imbricated pattern. The crystal structure of CPHB did not, however, strictly correspond to this view. We therefore undertook the investigation of three more cyano-compounds both in the solid and mesomorphic state. The compounds are members of the series 5-(4-R)-2-(4-cyanophenyl)pyrimidine, where R stands for *trans*-4-ethylcyclohexyl, -pentylcyclohexyl and -butylphenyl. Their names are abbreviated respectively as ECCPP, PCCPP and BPCPP. The mesomorphic behavior of BPCPP has been reported earlier,[6] and that of BPCPP will be reported elsewhere. In this paper we report the crystal structure of PCCPP and try to explain the mesomorphic organization in relation to its solid state packing and molecular interactions.

EXPERIMENTAL

The compound PCCPP has the following molecular structure and transition temperatures:



$$\mathrm{Cr} \underset{\sim 68^\circ\mathrm{C}}{\overset{100.6^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{N} \overset{234.9^\circ\mathrm{C}}{\rightleftharpoons} \mathrm{I}$$

Transparent, plate-shaped crystals were obtained by slow evaporation from a solution in acetone. The unit cell dimensions and space group were determined from oscillation and Weissenberg photographs. The crystals belong to the monoclinic system. The only systematic absences observed were those of the $h0l$ reflections, with odd values of h indicating unambiguously the space group $P2/a$. The density, measured by flotation indicated four molecules per unit cell.

A crystal of dimension (.04 × .28 × .45 mm^3) was used for the intensity data collection. Accurate cell parameters were determined by least squares fitting of $\sin\theta$ values for 24 strong reflections within the range $70 < 2\theta < 90$. Altogether 3277 intensities were measured on an Enraf Nonius CAD-4 diffractometer using graphite monochromated radiation in the interval $2.5 \leq \theta \leq 70°$ (h -25 to $+25$, k 0 to 10 and l 0 to 21). Of these, 2246 reflections were above the 2.5 $\sigma(I)$ level and were treated as observed. Structure factors from the intensities were derived in the usual way. Important crystallographic data are given in Table I.

STRUCTURE DETERMINATION AND REFINEMENT

The non-hydrogen atoms were found by direct methods, by means of the symbolic addition program system SIMPEL 83 (Kiers and Schenk, 1983)[7] using all reflections, in order to employ all positive and negative quartets, all signal relations, and all special two-dimensional quartets. The 300 strongest reflections were phased using

TABLE I

Important crystallographic data

Mol. Formula	$C_{22}H_{27}N_3$
Mol. Weight	333.48 g/mol.
Crystal system	Monoclinic
Space group	*P*2/*a*
a = 18.437(1) Å	
b = 7.1027(5) Å	
c = 15.342(1) Å	
β = 106.35 (5)°	
V = 1927.83 Å^3	
D_C = 1.15 g.cm^{-3}	
D_m = 1.17 g.cm^{-3}	
Z = 4	
λ(CuKα) = 1.5418 Å	
Number of independent reflections 3277	
Number of observed reflections 2246	

4 symbols. The highest CFOM revealed the complete structure. The trial structure was found to have an R value of 0.35, which after four cycles of refinement, reduced to 0.177 (using first an overall value and then individual values for isotropic temperature factors). The hydrogen atoms were found in a ΔF synthesis. The hydrogen atoms were given isotropic temperature factors and non-hydrogen atoms anisotropic temperature factors. Then the structure was refined through several cycles by block diagonal least squares. A weighting scheme with $w = (5.96 + F_{obs} + 0.0031\ F^2_{obs})^{-1}$ was applied. Extinction was taken into account with ext = 0.85. The calculations were carried out with XRAY76 (Stewart *et al.*).[8] The scattering factors were taken from Cromer and Mann.[9]

RESULTS AND DISCUSSIONS

Molecular Geometry and Conformation

Fig. 1 shows the perspective drawing of the molecule viewed normal to the least squares plane. Final positions and thermal parameters of all the atoms are listed in Tables II, III and IV using the numbering scheme shown in Fig. 1. Bond lengths and angles are given in Table V. The average C—C bond length in the phenyl ring (C1–C6) is 1.385(2) Å, the expected value[10] being 1.395 Å. The C—C bond lengths in the pyrimidine ring (C7–N2) are 1.374(2) Å and 1.381(2) Å, whereas the C—N bonds have the average value 1.336(2) Å, comparable to those found in other pyrimidine compounds.[11–13] The cyclohexyl group (C11–C16) has the average C—C bond length 1.530(3) Å which is reasonable.[14] The average C—C single bond length in the alkyl chain (C14–C22) is 1.516(3) Å which is lower by about 8σ than the expected[10] value 1.541 Å. The cyano-group bond length (C17–N3) is 1.142(3) Å which is close to the values found in other mesogenic compounds.[3,4,15,16] The

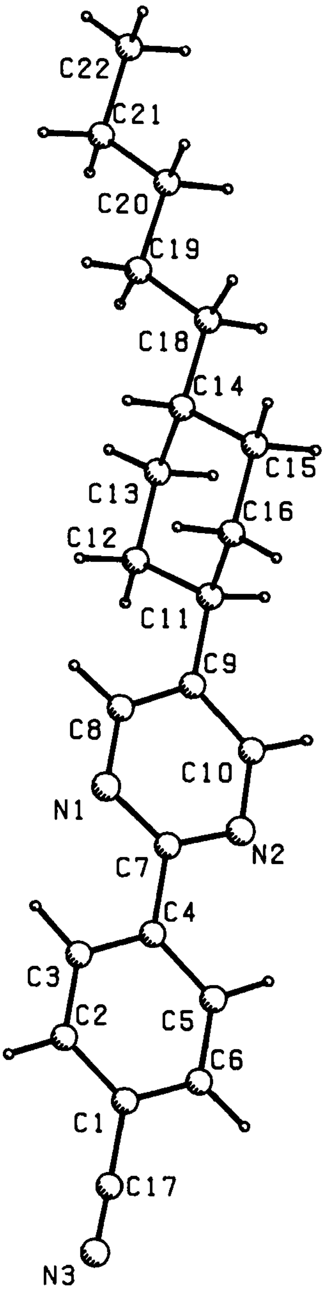


FIGURE 1 PCCPP molecule looking down the normal to the least squares along with the numbering scheme.

TABLE II

Fractional coordinates of the non-hydrogen atoms with e.s.d.'s in parentheses and equivalent isotropic thermal parameters. $Ueq = 1/3\ (U_{11}a^2a^{*2} + U_{22}b^2b^{*2} + U_{33}c^2c^{*2} + U_{13}aa^*cc^*\cos\beta)$

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	Ueq
C1	0.5925(1)	0.2702(3)	−0.0344(2)	0.060(1)
C2	0.5153(1)	0.2615(4)	−0.0779(2)	0.070(1)
C3	0.4647(1)	0.2477(3)	−0.0269(2)	0.064(1)
C4	0.4889(1)	0.2442(3)	0.0664(1)	0.055(1)
C5	0.5667(1)	0.2534(4)	0.1096(2)	0.068(1)
C6	0.6177(1)	0.2668(4)	0.0590(2)	0.069(1)
C7	0.4341(1)	0.2310(3)	0.1210(1)	0.056(1)
C8	0.3122(1)	0.2178(4)	0.1262(2)	0.070(1)
C9	0.3338(1)	0.2169(3)	0.2195(1)	0.060(1)
C10	0.4111(1)	0.2204(4)	0.2581(2)	0.071(1)
C11	0.2803(1)	0.2084(3)	0.2776(2)	0.064(1)
C12	0.2178(1)	0.3576(3)	0.2528(2)	0.071(1)
C13	0.1664(1)	0.3466(4)	0.3155(2)	0.075(2)
C14	0.1311(1)	0.1515(4)	0.3155(2)	0.066(1)
C15	0.1935(1)	0.0040(4)	0.3380(2)	0.079(2)
C16	0.2440(1)	0.0143(4)	0.2740(2)	0.075(2)
C17	0.6449(1)	0.2834(3)	−0.0883(2)	0.069(1)
C18	0.0824(1)	0.1378(4)	0.3813(2)	0.077(2)
C19	0.0130(1)	0.2619(4)	0.3598(2)	0.077(2)
C20	−0.0347(1)	0.2347(4)	0.4256(2)	0.073(2)
C21	−0.1003(1)	0.3684(4)	0.4102(2)	0.081(2)
C22	−0.1487(2)	0.3382(5)	0.4736(2)	0.095(2)
N1	0.36050(10)	0.2251(3)	0.0753(1)	0.066(1)
N2	0.46167(10)	0.2282(3)	0.2106(1)	0.071(1)
N3	0.6849(1)	0.2933(4)	−0.1330(2)	0.092(2)

average internal (C—C—C) bond angles in the phenyl ring is 120.0(2)°. In the pyrimidine ring the internal angles (N1—C7—N2, C9—C10—N2 and C1—C8—C9) have an average value 124.5(2)°, and the remaining three angles have an average value 115.4(2)°. The internal (C—C—C) angles in the cyclohexane ring vary from 108.9° to 112.2°, with an average of 110.9(2)° which is close to previously reported values. The external non-hydrogen angles in the phenyl ring have an average value of 120.4(2)° as expected. However, the angles C4—C7—N1 and C4—C7—N2 have values 117.1(2)° and 117.6(2)°, indicating a degree of strain between the phenyl and pyrimidine rings. Similarly the external angles C9—C11—C12 and C9—C11—C16 have values 113.4(2)° and 111.6(2)° respectively, indicating some strain between the pyrimidine and cyclohexane rings. The tetrahedral C—C—C bond angles in the alkyl chain range from 113.1° to 115.9°, with a mean value 114.2(2)° which exceeds the expected value by about 5°. The bond angle C1—C7—N3 is 178.2(2)°. Deviation from linearity of the cyano-bond has been found in other cyano-compounds[3,4,15,16]. The C—H distances range from 0.96 Å to 1.14 Å, with a mean value of 1.03(2) Å.

The length of the fully extended molecule, estimated from a stereo-model, is 21.2 Å, whereas the length of the molecule in the crystalline state is 20.7 Å. This indicates that in the crystalline state the molecule is in nearly its most extended form.

TABLE III

Anisotropic thermal parameters of the non-hydrogen atoms with the e.s.d.'s in parentheses. The temperature factor is of the form

$$\mathrm{Exp}[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$$

Atom	$U_{11}(\alpha)$	$U_{22}(\alpha)$	$U_{33}(\alpha)$	$U_{11}(\alpha)$	$U_{13}(\alpha)$	$U_{23}(\alpha)$
C1	0.056(1)	0.054(1)	0.080(1)	0.0026(10)	0.033(1)	−0.001(1)
C2	0.059(1)	0.087(2)	0.069(1)	−0.005(1)	0.026(1)	−0.006(1)
C3	0.050(1)	0.077(2)	0.071(1)	−0.002(1)	0.023(1)	−0.003(1)
C4	0.049(1)	0.048(1)	0.072(1)	0.0042(9)	0.0247(10)	0.000(1)
C5	0.051(1)	0.084(2)	0.073(1)	0.007(1)	0.022(1)	0.003(1)
C6	0.049(1)	0.079(2)	0.085(2)	0.005(1)	0.027(1)	0.003(1)
C7	0.050(1)	0.054(1)	0.069(1)	0.0047(9)	0.0220(10)	−0.002(1)
C8	0.051(1)	0.090(2)	0.074(1)	−0.001(1)	0.027(1)	−0.003(1)
C9	0.056(1)	0.062(1)	0.070(1)	0.003(1)	0.027(1)	−0.003(1)
C10	0.056(1)	0.097(2)	0.067(1)	0.009(1)	0.025(1)	−0.000(1)
C11	0.053(1)	0.079(2)	0.068(1)	0.003(1)	0.026(1)	−0.002(1)
C12	0.065(1)	0.066(1)	0.094(2)	0.003(1)	0.041(1)	0.002(1)
C13	0.066(1)	0.073(2)	0.100(2)	0.005(1)	0.047(1)	−0.001(1)
C14	0.055(1)	0.077(2)	0.072(1)	0.001(1)	0.026(1)	0.006(1)
C15	0.076(1)	0.077(2)	0.099(2)	0.010(1)	0.048(1)	0.014(1)
C16	0.076(1)	0.070(2)	0.093(2)	0.009(1)	0.046(1)	0.008(1)
C17	0.063(1)	0.068(1)	0.088(2)	0.002(1)	0.038(1)	−0.003(1)
C18	0.063(1)	0.093(2)	0.085(2)	0.007(1)	0.038(1)	0.013(1)
C19	0.059(1)	0.093(2)	0.088(2)	0.005(1)	0.036(1)	0.011(1)
C20	0.062(1)	0.082(2)	0.085(2)	0.002(1)	0.035(1)	0.003(1)
C21	0.066(1)	0.087(2)	0.102(2)	0.004(1)	0.040(1)	0.003(2)
C22	0.082(2)	0.109(2)	0.111(2)	0.010(2)	0.054(2)	0.001(2)
N1	0.0492(9)	0.083(1)	0.070(1)	−0.0015(9)	0.0242(9)	−0.003(1)
N2	0.0523(10)	0.096(2)	0.070(1)	0.008(1)	0.0245(9)	0.001(1)
N3	0.079(1)	0.102(2)	0.113(2)	0.001(1)	0.058(1)	0.000(1)

The least squares planes for different parts of the molecule have been calculated. The equation of the planes, individual and r.m.s. displacements of the constituent atoms have been listed in Table VI. The dihedral angles of these planes are also given in this table. As expected, the phenyl ring and the pyrimidine ring show a high degree of planarity, the dihedral angle being 2°. The cyano-group atoms C17 and N3 are displaced slightly downward from the plane of the phenyl ring. The cyclohexane ring is in the chair form. Three atoms are displaced upward from the plane and three are displaced downward. The displacements for C11 and C14 are approximately ±0.2 Å, for C12 and C15 ±0.4 Å and for C13 and C16 ±0.5 Å. The dihedral angle between the cyclohexane ring and the pyrimidine ring is 78.8°.

Molecular Packing

The packing of PCCPP molecules in the *ab* and *ac* planes is shown in Fig. 2 and Fig. 3 respectively. It can be seen that the phenyl and pyrimidine rings are almost in the *ac* plane, whereas the cyclohexane ring is almost in the *ab* plane. Pairs of molecules, related by a center of symmetry, give rise to a sheet of parallel molecules in the *ac* plane and these sheets are stacked in an imbricated fashion along the *b*-axis. The crystalline modification of PCCPP therefore corresponds to the commonly

TABLE IV

Fractional coordinates of the hydrogen atoms and isotropic thermal parameters with e.s.d.'s in parentheses. Atoms are numbered according to the heavy atoms to which they are attached.

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	U
H2	0.498(1)	0.265(3)	-0.148(1)	0.078(7)
H3	0.407(1)	0.241(3)	-0.057(2)	0.090(7)
H5	0.583(1)	0.248(3)	0.179(1)	0.074(6)
H6	0.673(1)	0.274(3)	0.092(1)	0.083(7)
H8	0.257(1)	0.211(3)	0.090(2)	0.089(7)
H10	0.433(1)	0.217(3)	0.326(1)	0.076(7)
H11	0.310(1)	0.227(3)	0.346(1)	0.068(6)
H14	0.098(1)	0.130(3)	0.249(1)	0.062(6)
H121	0.187(1)	0.344(3)	0.184(2)	0.084(7)
H122	0.244(1)	0.483(3)	0.258(1)	0.083(7)
H131	0.127(1)	0.444(4)	0.299(2)	0.095(8)
H132	0.198(1)	0.371(3)	0.385(2)	0.092(7)
H151	0.169(1)	-0.118(4)	0.336(2)	0.104(8)
H152	0.230(1)	0.025(4)	0.411(2)	0.094(8)
H161	0.211(1)	-0.009(3)	0.208(1)	0.074(6)
H162	0.284(1)	-0.078(4)	0.286(2)	0.111(9)
H181	0.065(1)	-0.001(4)	0.386(2)	0.101(8)
H182	0.117(1)	0.166(3)	0.447(2)	0.085(7)
H191	0.029(1)	0.397(4)	0.363(2)	0.096(8)
H192	-0.019(1)	0.239(3)	0.297(1)	0.082(7)
H201	0.001(1)	0.247(3)	0.496(2)	0.088(7)
H202	-0.055(1)	0.099(4)	0.422(2)	0.097(8)
H211	-0.133(1)	0.356(4)	0.340(2)	0.099(8)
H212	-0.078(2)	0.502(4)	0.419(2)	0.125(10)
H221	-0.169(1)	0.204(4)	0.466(2)	0.119(9)
H222	-0.117(1)	0.352(4)	0.541(2)	0.114(9)
H223	-0.191(2)	0.431(4)	0.465(2)	0.128(10)

TABLE V

Bond distances (Å) of the non-hydrogen atoms; standard deviations in parentheses.

C1—C2	1.393(2)	C10—N2	1.336(2)
C1—C6	1.377(2)	C11—C12	1.533(2)
C1—C17	1.441(2)	C11—C16	1.527(2)
C2—C3	1.380(2)	C12—C13	1.531(3)
C3—C4	1.374(2)	C13—C14	1.531(3)
C4—C5	1.402(2)	C14—C15	1.522(3)
C4—C7	1.486(2)	C14—C18	1.531(2)
C5—C6	1.381(2)	C15—C16	1.533(3)
C7—N1	1.341(2)	C17—N3	1.142(3)
C7—N2	1.325(2)	C18—C19	1.512(3)
C8—C9	1.374(2)	C19—C20	1.526(3)
C8—N1	1.341(2)	C20—C21	1.503(3)
C9—C10	1.381(2)	C21—C22	1.509(3)
C9—C11	1.505(2)		

Bond distances (Å) of the hydrogen atoms; standard deviations in parentheses.

C2—H2	1.03(1)	C16—H161	1.04(1)
C3—H3	1.03(2)	C16—H162	0.96(2)
C5—H5	1.02(1)	C18—H181	1.05(2)
C6—H6	1.00(2)	C18—H182	1.05(2)
C8—H8	1.01(2)	C19—H191	1.00(2)
C10—H10	1.01(1)	C19—H192	0.99(2)
C11—H11	1.05(1)	C20—H201	1.10(2)

TABLE V *continued*

C12—H121	1.05(2)	C20—H202	1.03(2)
C12—H122	1.01(2)	C21—H211	1.08(2)
C13—H131	0.98(2)	C21—H212	1.03(2)
C13—H132	1.08(2)	C22—H221	1.02(2)
C14—H14	1.04(1)	C22—H222	1.04(2)
C15—H151	0.97(2)	C22—H223	1.00(2)
C15—H152	1.14(2)		

Bond angles (°) of the non hydrogen atoms; standard deviations in parentheses.

C2—C1—C6	119.9(2)	C9—C11—C12	113.4(2)
C2—C1—C17	119.9(2)	C9—C11—C16	111.6(2)
C6—C1—C17	120.9(2)	C12—C11—C16	108.9(2)
C1—C2—C3	119.6(2)	C11—C12—C13	111.3(2)
C2—C3—C4	121.3(2)	C12—C13—C14	112.6(2)
C3—C4—C5	118.7(2)	C13—C14—C15	109.2(2)
C3—C4—C7	121.0(2)	C13—C14—C18	112.7(2)
C5—C4—C7	120.3(2)	C15—C14—C18	110.7(2)
C4—C5—C6	120.4(2)	C14—C15—C16	112.2(2)
C1—C6—C5	120.2(2)	C11—C16—C15	111.0(2)
C4—C7—N1	117.1(2)	C1—C17—N3	178.2(2)
C4—C7—N2	117.6(2)	C14—C18—C19	115.9(2)
N1—C7—N2	125.3(2)	C18—C19—C20	113.1(2)
C9—C8—N1	124.2(2)	C19—C20—C21	113.8(2)
C8—C9—C10	114.1(2)	C20—C21—C22	113.9(2)
C8—C9—C11	124.8(2)	C7—N1—C8	115.9(2)
C10—C9—C11	121.1(2)	C7—N2—C10	116.3(2)
C9—C10—N2	124.1(2)		

Bond angles (°) of the hydrogen atoms; standard deviations in parentheses.

C1—C2—H2	118(1)	H151—C15—H152	107(2)
C3—C2—H2	122(1)	C11—C16—H161	108(1)
C2—C3—H3	122(1)	C11—C16—H162	108(2)
C4—C3—H3	117(1)	C15—C16—H161	109(1)
C4—C5—H5	117(1)	C15—C16—H162	114(1)
C6—C5—H5	123(1)	H161—C16—H162	107(2)
C1—C6—H6	121(1)	C14—C18—H181	111(1)
C5—C6—H6	118(1)	C14—C18—H182	108(1)
C9—C8—H8	121(1)	C19—C18—H181	108(1)
N1—C8—H8	114(1)	C19—C18—H182	110(1)
C9—C10—H10	121(1)	H181—C18—H182	103(2)
N2—C10—H10	115(1)	C18—C19—H191	109(1)
C9—C11—H11	110(1)	C18—C19—H192	111(1)
C12—C11—H11	108(1)	C20—C19—H191	108(1)
C16—C11—H11	105(1)	C20—C19—H192	109(1)
C11—C12—H121	110(1)	H191—C19—H192	107(2)
C11—C12—H122	106(1)	C19—C20—H201	110(1)
C13—C12—H121	112(1)	C19—C20—H202	111(1)
C13—C12—H122	111(1)	C21—C20—H201	110(1)
H121—C12—H122	106(2)	C21—C20—H202	109(1)
C12—C13—H131	110(1)	H201—C20—H202	104(2)
C12—C13—H132	111(1)	C20—C21—H211	108(1)
C14—C13—H131	111(1)	C20—C21—H212	107(2)
C14—C13—H132	105(1)	C22—C21—H211	111(1)
H131—C13—H132	107(2)	C22—C21—H212	110(1)
C13—C14—H14	105(1)	H211—C21—H212	107(2)
C15—C14—H14	109(1)	C21—C22—H221	109(2)
C18—C14—H14	110(1)	C21—C22—H222	111(1)
C14—C15—H151	107(2)	C21—C22—H223	114(2)
C14—C15—H152	109(1)	H221—C22—H222	107(2)
C16—C15—H151	112(1)	H221—C22—H223	111(2)
C16—C15—H152	109(1)	H22—C22—H223	106(2)

TABLE VI

Equations of least squares planes, the individual, and r.m.s. displacements (in Å) of the atoms from them.

Equations of the planes	Atoms		r.m.s.
1. $-0.0677x + 0.9974y + 0.0246z = 1.156$	C1	−0.0044	0.0036
	C2	0.0018	
	C3	0.0063	
	C4	−0.0024	
	C5	0.0032	
	C6	0.0012	
Other atoms	C17	−0.0054	0.0136
	N3	−0.0184	
2. $-0.0365x + 0.9992y + 0.0131z = 1.384$	C7	0.0058	0.0050
	C8	−0.0040	
	C9	0.0077	
	C10	−0.0059	
	N1	−0.0025	
	N2	−0.0012	
3. $0.0106x + 0.1891y + 0.9819z = 4.5425$	C11	−0.2060	0.3882
	C12	−0.3757	
	C13	0.5024	
	C14	0.2332	
	C15	0.3720	
	C16	−0.5259	

Dihedral angle between plane 1 and plane 2 is 2.0°, and between plane 3 and plane 2 is 78.8°.

found molecular packing in a nematogen. With increase in thermal energy, the transformation to the liquid crystal state is presumably accomplished by the breakdown of the molecular stacking along the *b*-axis. This gives rise to three translational degrees of freedom of the pairs of parallel molecules accompanied by rotation about the long molecular axis. The transition is thus of the displacive type.[5]

All interatomic contact distances less than 4 Å involving non-hydrogen atoms only, have been listed in Table VII. We note that only the distance between the atom C6 of the molecule at x, y, z and the atom N3 of the molecule at $1 + \frac{1}{2} - x$, y, $\bar{z}$ is close to the sum of the Van der Waal's radii of the atoms. The length of this pair of molecules, in head to head configuration, is 39.8 Å. On the other hand, the apparent length of the molecule in the nematic state is found to be 26.2 Å,

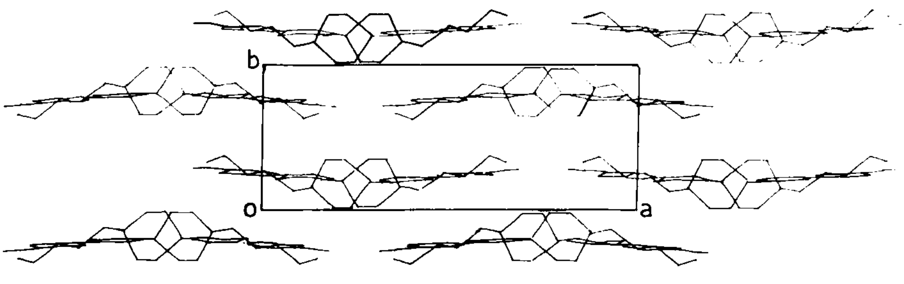


FIGURE 2 Crystal structure of PCCPP in *ab* plane.

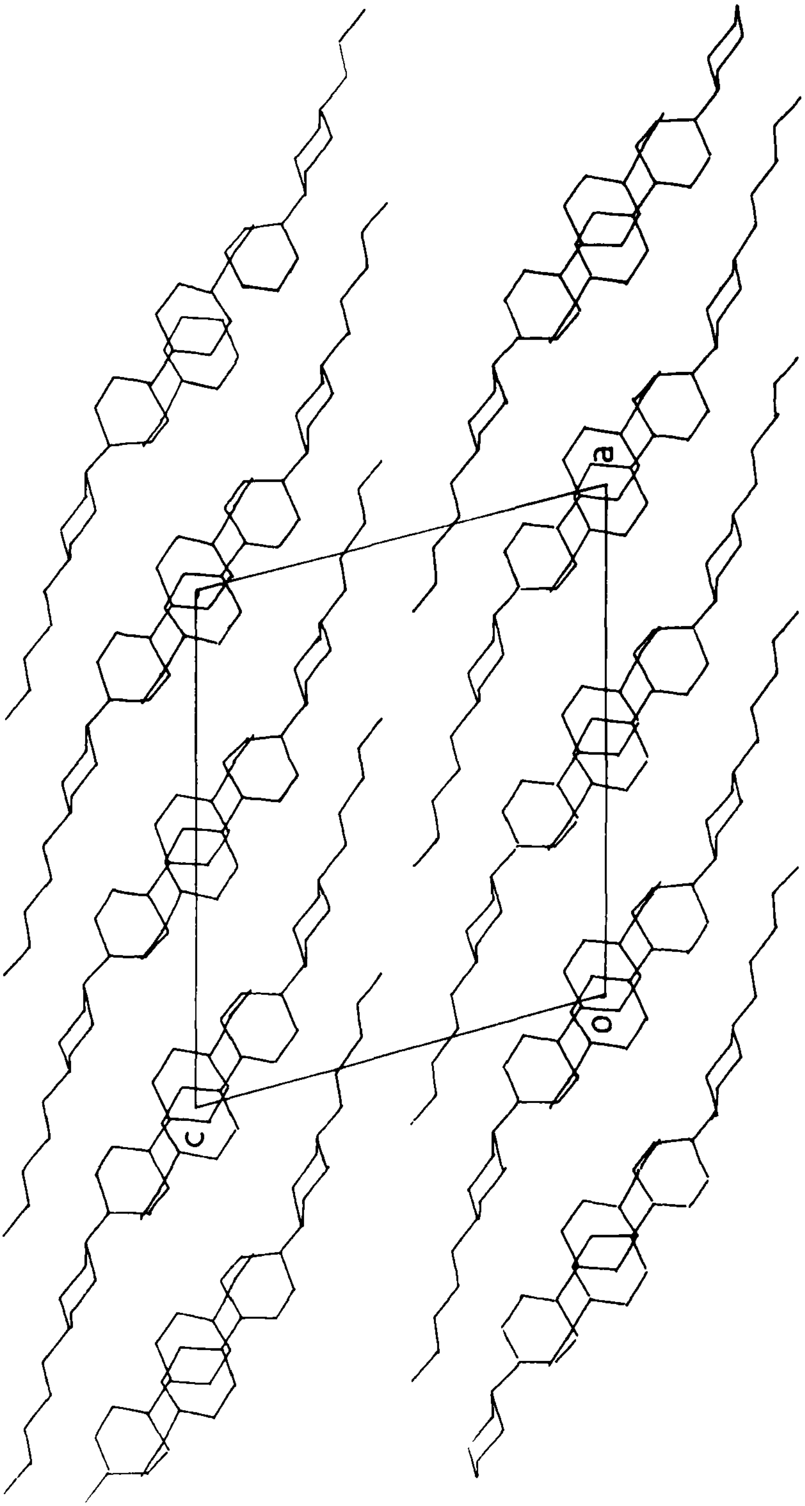


FIGURE 3 Crystal structure of PCCPP in *ac* plane.

TABLE VII

Intermolecular contact distances less than 4 Å (involving nonhydrogen atoms)

C1—C3^b	3.779	C6—C16^e	3.996
C1—C4^a	3.928	C6—N3^d	3.499
C1—C4^b	3.738	C7—C17^a	3.913
C1—C7^a	3.783	C7—C17^b	3.723
C1—C7^b	3.767	C8—C8^c	3.906
C1—N1^a	3.718	C8—C17^a	3.728
C1—N1^b	3.782	C8—C17^b	3.711
C2—C3^a	3.933	C8—N1^c	3.762
C2—C3^b	3.813	C8—N3^a	3.632
C2—C4^a	3.598	C8—N3^b	3.474
C2—C4^b	3.517	C9—N3^a	3.841
C2—C5^a	3.935	C9—N3^b	3.705
C2—C5^b	3.739	C10—C21^f	3.781
C2—C7^a	3.727	C10—C21^g	3.781
C2—C7^b	3.827	C11—C21^f	3.937
C2—C14^c	3.955	C11—C21^g	3.937
C3—C3^a	3.762	C12—N3^b	3.821
C3—C3^b	3.823	C15—C22^e	3.911
C3—C4^a	3.688	C16—N3^a	3.573
C3—C4^b	3.797	C17—N1^a	3.620
C3—C5^a	3.768	C17—N1^b	3.500
C3—C5^b	3.753	C17—N3^d	3.922
C3—C6^a	3.935	C18—N2^e	3.910
C3—C6^b	3.744	N1—N3^a	3.932
			3.688

None: $x\ y\ z$ a: $1 - x, \bar{y}, \bar{z}$ b: $1 - x, 1 - y, \bar{z}$ c: $\frac{1}{2} - x, y, \bar{z}$,
d: $1 + \frac{1}{2} - x, y, \bar{z}$ e: $\frac{1}{2} + x, \bar{y}, z$ f: $\frac{1}{2} + x - 1, 1 - y, z$
g: $1/2 + x, 1 - y, z$.

which is 1.2 times the most extended molecular length. This is often found in cyano-compounds and to explain this a bimolecular association of the molecules, because of cyano-group interactions, is invoked.[3,6,16–18] We therefore infer that interaction between dipoles of cyano-groups exists both in the crystalline and nematic phase. In the crystalline state, the overlap of the molecules is small (in cyano-region only) due to steric hindrance, and in the nematic state this hindrance is overcome by the increased thermal motions giving rise to a large overlap (including both the cyano and the pyrimidine ring).

References

1. A. J. Leadbetter and M. A. Mazid, *Mol. Cryst. Liq. Cryst.*, **65**, 265 (1981).
2. U. Baumeister, H. Hartung, M. Gdaniec and M. Jaskolski, *Mol. Cryst. Liq. Cryst.*, **69**, 119 (1981).
3. P. Mandal and S. Paul, *Mol. Cryst. Liq. Cryst.*, **131**, 223 (1985).
4. P. Mandal, S. Paul, H. Schenk and K. Goubitz, *Mol. Cryst. Liq. Cryst.*, **135**, 35 (1986).
5. R. F. Bryan, *Proc. Pre-congress Symposium on Organic Crystal Chemistry*, Poznan, Poland (1979).
6. B. Jha, A. Nandi, S. Paul and R. Paul, *Mol. Cryst. Liq. Cryst.*, **104**, 289 (1984).
7. C. T. Kiers and H. Schenk, SIMPEL (83). An automatic direct method program package, University of Amsterdam, 1983; H. Schenk, *Recl. Trav. Chim. Pays. Bas* **102**, 1 (1983).
8. J. M. Stewart, The XRAY 76 System, Tech. Rep., TR-446 Computer Science Center, University of Maryland, College Park, Maryland (1976).

9. D. T. Cromer and J. B. Mann, *Acta Cryst.*, **A24**, 321 (1968).
10. International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham, 1962.
11. C. J. B. Clews and W. Cochran, *Acta Cryst.*, **2**, 46 (1949).
12. G. S. Parry, *Acta. Cryst.*, **7**, 313 (1954).
13. H. G. Beaton, G. R. Willey and M. G. B. Drew, *J. Chem. Soc. Perkin Trans II, No. 4*, 469 (1987).
14. S. Bhattacharjee and G. A. Jeffrey, *Mol. Cryst. Liq. Cryst.*, **101**, 247 (1983).
15. U. Baumeister, H. Hartung and M. Jaskolski, *Mol. Cryst. Liq. Cryst.*, **88**, 167 (1982); **69**, 119 (1981).
16. W. Haase, H. Paulus and H. T. Muller, *Mol. Cryst. Liq. Cryst.*, **97**, 131 (1983).
17. B. Bhattacharjee, S. Paul and R. Paul, *Mol. Cryst. Liq. Cryst.*, **89**, 181 (1982).
18. A. J. Leadbetter, R. M. Richardson and C. N. Colling, *J. Phys.* (*Paris*), **36**, 37 (1975).