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The molecular and crystal structure of bipolar, mesogenic biphenyls: a comparison of similar compounds $HO(CH_2)_6OC_6H_4C_6H_4R$ with R = cyano and nitro terminal groups

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The crystal and molecular structures of 4,4′-disubstituted biphenyls of formula $HO(CH_2)_6OC_6H_4C_6H_4R$ with R = cyano and nitro terminal groups have been determined including co-crystallized materials of both of the compounds. The extended molecules arrange in an antiparallel fashion with dipole–dipole interactions, exhibiting a sheet-like structure for the compound with the cyano terminal group, and for the other two materials an extended head to tail string-like structure caused by dipolar interaction, also packed in sheets in an antiparallel fashion by van der Waals interactions. Knowledge of the interaction of the compounds in the crystalline state serves as a prerequisite for the determination of interactions in the liquid crystalline state of the same or similar compounds.

1. Introduction

In previous work [1], the arrangements of a homologous series of bipolar mesogenic biphenyls with cyano terminal groups were determined and discussed and different packings detected for compounds with short and long alkyl terminal groups. However, the compound with a terminal alkyl chain length of $n = 6$, the link between these two different packing arrangements, could not be solved because of difficulties in obtaining a phasing model with the available software. Evaluation of the X-ray intensities from a single crystal, now with SIR 97 [2], immediately led to a phasing model. A refinement was undertaken and the structure compared with the previously published ones. Further, since we also collected data for the similar biphenyl compound with a nitro terminal group, and in addition were able to co-crystallize both compounds with nitro and cyano terminal groups, we are in the position to evaluate the influence of various polar interactions on the arrangements of these structures. These interactions can now be studied by spectroscopic means and compared with the interactions in the liquid crystalline state [3].

2. Experimental, structure solution and refinement

Crystals suitable for an X-ray determination were obtained by slow crystallization from butyl acetate solutions of 4-(6-hydroxyhexyloxy)-4′-cyanobiphenyl (H6CBP), 4-(6-hydroxyhexyloxy)-4′-nitrobiphenyl (H6NBP) and a mixture of H6CBP/H6NBP, mole fraction of (H6NBP) = 0.6, at room temperature. The phase sequence for H6CBP has been determined as Cr_2 91.9 N 110.3 I, with respect to Cr_1 94.8 N 110.3 I and on cooling I 110 N 80–82 Cr_1 (°C) [3]. Only a nematic liquid crystalline phase is observed, but the different crystalline phases Cr_1 or Cr_2 are obtained when crystallizing from the melt or from solution. Data collection was performed on a CAD4 single crystal diffractometer with MoK_α or CuK_α radiation and data processing and refinement against F with the MolEN package of Enraf Nonius, Delft [4]. The starting model for H6CBP was produced by SIR 97 [2]. The hydrogen atoms have been placed at respective sites and not refined as well as their isotropic B values. Difference Fourier analysis led to the position of the hydroxyl hydrogen. Table 1 represents the basic crystallographic data. The figures representing conformation and packing of the structures were produced with SCHAKAL 92 [5]. The high R-value of the co-crystallized materials was caused by some disorder in the alkoxy chain which also led to broad reflections.

3. Results and discussion

3.1. *Molecular geometry and conformation*

Figure 1 (*a–c*) represents the molecular structures and the numbering schemes of the non-hydrogen atoms for H6CBP and H6NBP, as well as for the co-crystallized materials H6CBP(0.35)/H6NBP(0.65). This ratio was

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Table 1. Summary of crystallographic data.

Parameter	H6CBP	H6CBP/H6NBP	H6NBP
Molecular formula	$C_{19}H_{21}NO_2$	$C_{19}H_{21}NO_2 \times 0.65C_{18}H_{21}NO_4$	$C_{18}H_{21}NO_4$
Formula weight/g mol^{-1}	295.35	309.37	315.37
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
Number in Int. Tables	2	2	2
a/Å	9.747(7)	7.097(2)	7.125(2)
b/Å	14.020(8)	9.943(3)	9.769(2)
c/Å	14.219(8)	12.408(4)	12.257(2)
α/°	113.35(3)	105.92(2)	103.17(1)
β/°	102.93(4)	91.73(2)	91.58(2)
γ/°	102.95(4)	102.58(2)	100.06(2)
V/Å^3	1629(2)	818.0(5)	815.9(4)
D_{cal}/g cm^{-3}	1.204	1.26	1.28
Z (asymmetric unit)	4	2	2
μ (MoK$_\alpha$/CuK$_\alpha$)/cm^{-1}	0.7	0.8	7.0
λ (MoK$_\alpha$/CuK$_\alpha$)/Å	0.71073	0.71073	1.54184
Number of reflections used for lattice parameter refinement	20	24	17
Scan range	$8° < \theta < 14°$	$8° < \theta < 20°$	$19° < \theta < 31°$
F(000)	632	329	336
Reflections collected	3747	2350	1844
Unique data	3483	2138	1666
Significant I's ($>3\sigma$)	2103	1198	1297
Data collection	$1° \leqslant \theta \leqslant 21°$	$1° \leqslant \theta \leqslant 25°$	$2° \leqslant \theta \leqslant 50°$
Parameters refined	397	217	208
R	0.038	0.076	0.046
R_w	0.048	0.099	0.070
Highest peak in $\Delta\rho$/e Å^{-3}	0.13(3)	0.27(7)	0.14(3)
Crystal colour	yellow-brown	yellow-brown	colourless
Crystal size	platelet	platelet	rod-like

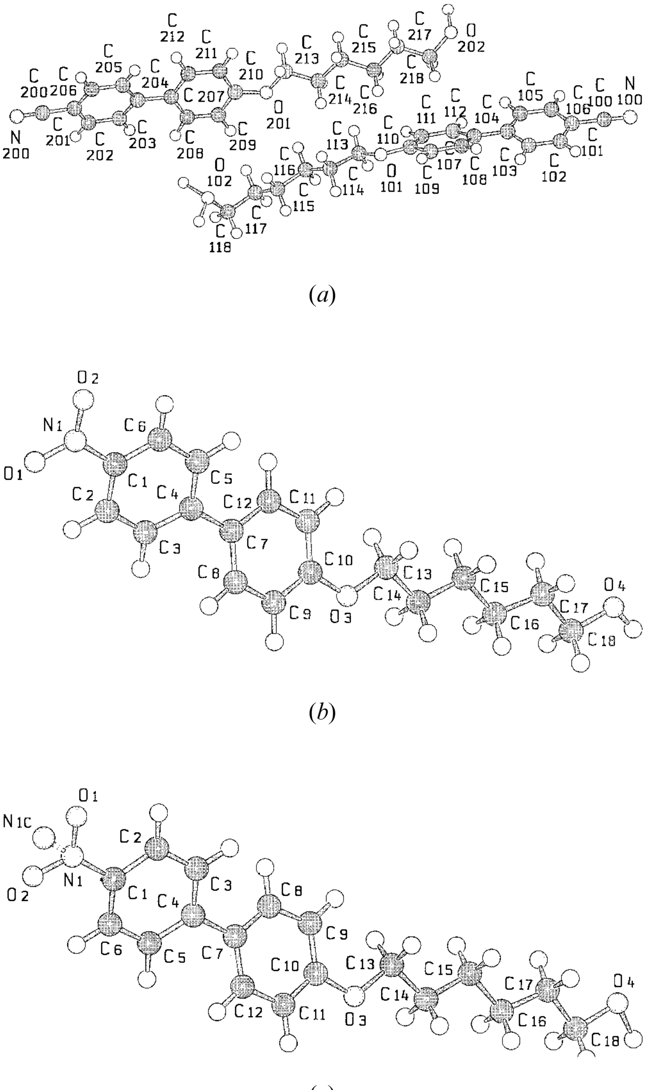
determined by evaluating the partial occupancy of the oxygen of the nitro group and the nitrogen of the cyano group. The original solution from which the co-crystallization took place contained a molar fraction 0.6 of H6NBP. The fractional coordinates of the structures are listed in table 2.

All the compounds crystallize in an extended conformation with the alkyl chain in an all-*trans*-conformation. H6CBP contains two molecules, 1 and 2, of slightly different conformations in the asymmetric unit of space group P-1 exhibiting different torsion angles of the hydroxyl oxygen τ(C116–C117–C118–O102) = 67.4°(4) and τ(C216–C217–C218–O202) = 173.3°(3). Only one molecule was detected in the asymmetric unit of space group P-1 for the other two materials with consequences for the arrangements of the molecules in the crystallites. Here, the torsion angles describing the position of the hydroxyl oxygen were determined to be $\tau = 176.7°(3)$ for H6NBP and $\tau = 178.9°(6)$ for the co-crystallized materials. The lengths of the two independent molecules in H6CBP differ slightly, and are 18.7 Å for molecule 1 and 19.2 Å for molecule 2 measured from the cyano to the hydroxyl group, N1 to O2; the length for H6NBP amounts to 18.8 Å from the oxygen of the nitro group to the hydroxyl group, O1 … O4.

The two best planes describing the two rings A and B of the biphenyl system for H6CBP are twisted for molecule 1 by 19.6°(2)° and for molecule 2 by 15.9°(1), but in opposite directions from molecule 1 clearly expressed by the two torsion angles τ(C105–C104–C107–C112) = 19.3°(5) and τ(C205–C204–C207–C212) = −15.4°(4). The two rings A and B are twisted by 23.2°(2) for H6NBP and 24.5°(4) for the co-crystallized materials. The data for the bond lengths and angles for all materials investigated agree closely with those found for other compounds of the type H*n*CBP [1]. The somewhat smaller bond angles with considerable deviations from the expected 120° in the biphenyl rings for C3–C4–C5 and C8–C7–C12 are found in the two molecules of the asymmetric unit for H6CBP, as well as in the two other materials as already pointed out and discussed in earlier papers for similar materials [1, 6].

3.2. *Packing arrangement and hydrogen bonding*

The packing of the H6CBP molecules compares to some extent with that for the higher homologues of the



(a)

(b)

(c)

Figure 1. Representation of the molecules and atom labelling of (a) H6CBP, partial occupancy of hydroxyl hydrogen, (b) H6NBP and (c) co-crystallized H6CBP/H6NCP, partial occupancy of N1C, O1, O2.

series HnCBP ($n \geqslant 7$) with hydrogen bonding in the *ac* plane along the *a* direction (figure 2, table 3). All the hydroxyl oxygens are interconnected by hydrogen bonds in a line from which the molecules stick out on both sides. It seems that dimers are formed by the hydrogen bonds and these are connected by further hydrogen bonding to the next dimers in the *a* direction thus forming a limited two-dimensional sheet of molecules. The terminal cyano groups of these limited sheets interact by polar forces perpendicular to the sheet discussed and create a widespread two-dimensional sheet with a variation in sheet thickness, figure 2(*b*), table 3. The shortest distance between the nitrogen atoms involves the two independent molecules 1 and 2, with N100 … N200′

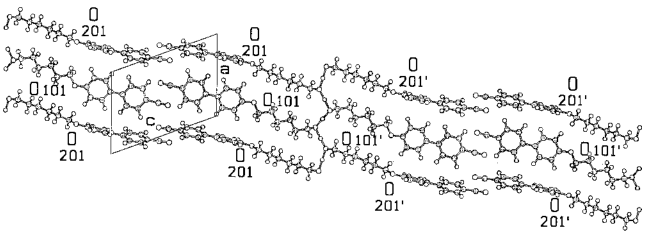
Table 2. Fractional coordinates and isotropic displacement parameters B_{eq}. Estimated standard deviations in parentheses. $B_{eq} = (4/3)\,[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)\,B(1,2) + ac(\cos\beta)\,B(1,3) + bc(\cos\alpha)\,B(2,3)]$.

Atom	*x*	*y*	*z*	$B/\text{Å}^2$
H6CBP				
O101	−0.0027(2)	0.0136(2)	0.3489(1)	5.19(6)
O102	0.5733(3)	0.4542(2)	0.9310(2)	6.44(7)
O201	0.4809(2)	0.0297(2)	0.6675(1)	5.46(6)
O202	−0.1218(2)	−0.4821(2)	0.0332(2)	6.57(7)
N100	−0.6524(3)	−0.4334(2)	−0.5349(2)	7.1(1)
N200	1.1152(3)	0.4183(2)	1.5501(2)	6.96(9)
C100	−0.5813(3)	−0.3901(2)	−0.4439(2)	4.99(9)
C200	1.0567(3)	0.3780(2)	1.4573(2)	5.2(1)
C101	−0.4925(3)	−0.3337(2)	−0.3297(2)	4.03(8)
C102	−0.5601(3)	−0.3068(2)	−0.2527(2)	4.82(9)
C103	−0.4757(3)	−0.2512(2)	−0.1433(2)	4.64(9)
C104	−0.3201(3)	−0.2215(2)	−0.1059(2)	3.62(8)
C105	−0.2539(3)	−0.2489(2)	−0.1856(2)	4.87(9)
C106	−0.3374(3)	−0.3038(2)	−0.2950(2)	5.0(1)
C107	−0.2314(3)	−0.1627(2)	0.0117(2)	3.71(8)
C108	−0.2977(3)	−0.1643(2)	0.0885(2)	4.71(9)
C109	−0.2193(3)	−0.1067(2)	0.1986(2)	4.84(9)
C110	−0.0686(3)	−0.0446(2)	0.2376(2)	4.12(8)
C111	0.0031(3)	−0.0439(2)	0.1644(2)	4.73(9)
C112	−0.0793(3)	−0.1027(2)	0.0529(2)	4.48(9)
C113	0.1503(3)	0.0877(2)	0.3953(2)	5.1(1)
C114	0.1826(3)	0.1560(2)	0.5159(2)	5.05(9)
C115	0.3404(4)	0.2411(3)	0.5735(2)	6.1(1)
C116	0.3717(3)	0.3238(2)	0.6915(2)	5.3(1)
C117	0.5225(4)	0.4145(3)	0.7434(2)	6.3(1)
C118	0.5567(4)	0.4990(3)	0.8578(3)	7.0(1)
C201	0.9820(3)	0.3260(2)	1.3413(2)	4.18(8)
C202	0.9919(3)	0.3853(2)	1.2838(2)	4.82(9)
C203	0.9164(3)	0.3341(2)	1.1729(2)	4.65(9)
C204	0.8255(3)	0.2218(2)	1.1152(2)	3.75(8)
C205	0.8189(3)	0.1629(2)	1.1742(2)	4.36(9)
C206	0.8955(3)	0.2137(2)	1.2854(2)	4.39(9)
C207	0.7388(3)	0.1689(2)	0.9971(2)	3.60(8)
C208	0.7144(3)	0.2314(2)	0.9438(2)	4.64(9)
C209	0.6297(3)	0.1827(2)	0.8351(2)	4.99(9)
C210	0.5658(3)	0.0688(2)	0.7741(2)	4.09(8)
C211	0.5903(3)	0.0040(2)	0.8236(2)	4.81(9)
C212	0.6750(3)	0.0546(2)	0.9333(2)	4.70(9)
C213	0.4018(3)	−0.0861(2)	0.6014(2)	4.91(9)
C214	0.2955(4)	−0.1031(2)	0.4969(2)	5.2(1)
C215	0.2109(3)	−0.2226(2)	0.4141(2)	5.3(1)
C216	0.1022(3)	−0.2373(2)	0.3105(2)	5.06(9)
C217	0.0315(4)	−0.3567(2)	0.2218(2)	5.4(1)
C218	−0.0713(4)	−0.3703(3)	0.1185(2)	5.8(1)
H12O	0.729	0.478	0.982	7.0
H22O	0.000	−0.500	0.000	7.0
H32O	0.500	0.500	1.000	7.0
H6NBP				
O1	−0.9821(3)	0.2304(2)	1.5366(2)	6.48(6)
O2	−0.7573(3)	0.4152(2)	1.5698(2)	7.15(7)
O3	0.0547(3)	−0.2661(2)	1.0876(2)	5.56(5)
O4	0.9995(3)	−0.4047(2)	0.6933(2)	8.85(8)
N1	−0.8186(3)	0.2878(3)	1.5262(2)	5.18(7)
C1	−0.6913(4)	0.2047(3)	1.4627(2)	4.23(7)
C2	−0.7547(4)	0.0607(3)	1.4156(2)	4.44(7)
C3	−0.6320(4)	−0.0158(3)	1.3551(2)	4.37(7)

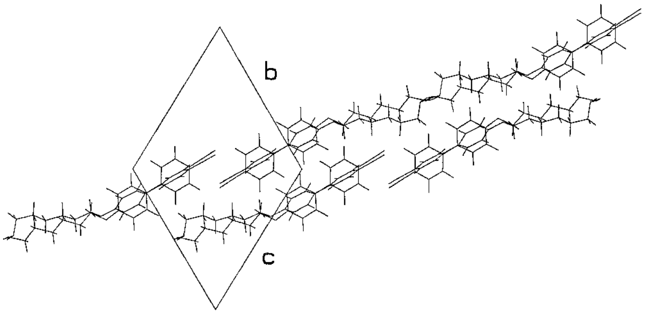
Table 2. (*continued*).

Atom	x	y	z	B/Å^2
C4	−0.4471(4)	0.0477(3)	1.3386(2)	3.84(7)
C5	−0.3888(4)	0.1941(3)	1.3895(3)	4.68(8)
C6	−0.5086(4)	0.2725(3)	1.4509(3)	4.73(8)
C7	−0.3178(4)	−0.0335(3)	1.2710(2)	3.91(7)
C8	−0.3371(4)	−0.1821(3)	1.2528(2)	4.67(8)
C9	−0.2124(4)	−0.2552(3)	1.1931(3)	4.94(8)
C10	−0.0619(4)	−0.1841(3)	1.1460(2)	4.28(7)
C11	−0.0392(4)	−0.0366(3)	1.1611(3)	4.59(8)
C12	−0.1643(4)	0.0364(3)	1.2231(3)	4.39(7)
C13	0.2136(4)	−0.1995(3)	1.0384(3)	4.75(8)
C14	0.3049(4)	−0.3151(3)	0.9711(3)	5.42(8)
C15	0.4847(4)	−0.2613(3)	0.9218(3)	5.09(8)
C16	0.5693(4)	−0.3813(3)	0.8508(3)	5.55(9)
C17	0.7550(4)	−0.3376(3)	0.8067(3)	5.22(8)
C18	0.8301(4)	−0.4602(3)	0.7348(3)	6.20(9)
H4O	1.055(4)	−0.475	0.659	7.0
H6CBP(0.35)/H6NBP(0.65)				
O1	−0.7451(9)	0.4087(7)	0.5720(6)	12.0(2)
O2	−0.9736(8)	0.2242(7)	0.5292(6)	10.1(2)
O3	−0.0679(5)	−0.2601(3)	0.0901(3)	7.17(9)
O4	−0.9912(7)	−0.4177(5)	−0.2977(5)	13.2(2)
N1	−0.8106(7)	0.2811(5)	0.5183(4)	8.7(2)
N1C	−0.917(2)	0.351(2)	0.561(1)	15.7(5)
C1	−0.6819(6)	0.1969(5)	0.4558(4)	6.5(1)
C2	−0.4964(7)	0.2721(6)	0.4457(5)	7.7(2)
C3	−0.3760(7)	0.1964(5)	0.3850(4)	6.9(1)
C4	−0.4342(6)	0.0488(5)	0.3363(4)	5.6(1)
C5	−0.6164(7)	−0.0195(5)	0.3521(4)	6.7(1)
C6	−0.7392(7)	0.0554(6)	0.4114(4)	6.9(1)
C7	−0.3029(6)	−0.0296(5)	0.2703(4)	5.5(1)
C8	−0.1539(6)	0.0367(5)	0.2182(4)	6.0(1)
C9	−0.0275(7)	−0.0337(5)	0.1579(4)	6.1(1)
C10	−0.0476(7)	−0.1760(5)	0.1476(4)	6.0(1)
C11	−0.1945(7)	−0.2484(5)	0.1970(4)	7.0(1)
C12	−0.3165(7)	−0.1745(5)	0.2571(4)	6.6(1)
C13	0.2241(7)	−0.1939(5)	0.0383(4)	5.9(1)
C14	0.3185(7)	−0.3104(5)	−0.0239(5)	7.2(2)
C15	0.4925(7)	−0.2571(5)	−0.0776(4)	6.8(1)
C16	0.5750(8)	−0.3832(6)	−0.1448(5)	8.6(2)
C17	0.7525(7)	−0.3445(6)	−0.1900(5)	7.9(2)
C18	0.8207(8)	−0.4741(6)	−0.2574(6)	10.0(2)
H4O	1.045	−0.509	0.355	8.0

equal to 3.47 Å. The sheets above and below are stacked by loose van der Waals interactions, in contrast to the longer homologues where at least one strong polar interaction connects these sheets. Further differences in comparison with the longer homologues are caused by the fact that two independent molecules 1 and 2 are present in the asymmetric unit of H6CBP, these being twisted, e.g. with their A planes at 72.6 (2)°, almost perpendicular to each other—cf. figure 2 (*b*)—in contrast to the higher homologues where the A planes of all the molecules lie almost coplanar. A projection down the molecular axis reveals that each molecule is surrounded by six nearest neighbours with two of the them pointing in the same direction and four in the opposite direction (see figure 3).



(*a*)



(*b*)

Figure 2. Representation of the packing of H6CBP in two projections in direction (*a*) [0 1 0] and (*b*) [1 0 0] to show the strong polar interactions.

The crystals of H6NCP and the co-crystallized materials are isomorphous and the molecules are arranged in the same manner when compared with one another, but differ considerably from H6CBP as expected. The molecules are interconnected by hydrogen bonds in a head to tail fashion and form an infinite string as demonstrated for the co-crystallized materials in figure 4. Between the strings (molecules), which are also arranged in sheets, only van der Waals interactions are present (figure 5). Only minor deviations are detected for H6NCP as compared with the co-crystallized materials, and show up in the hydrogen bond length (but may not be visualized in a drawing) and give rise to a complex interaction scheme for both compounds (cf. table 3). However, the co-crystallized materials exhibit some disorder of the hydroxyl oxygen position and the alkyl chain detected by difference Fourier analysis. The packing arrangement viewed down the molecular axis resembles very much, in an overall view, that of H6CBP, with rows being identified (figure 6). On one of the rows all the molecules point in one direction, and on the next parallel row in the opposite direction. Rows almost perpendicular to those mentioned contain molecules with adjacent molecules pointing in opposite directions.

Table 3. Hydrogen bonds and strong polar interactions for H6CBP, H6NCP and co-crystallized materials of both compounds (cf. figures 2, 4). Oxygen–oxygen and nitrogen–nitrogen distances are listed (in Å), as well as the distances and angles involving the attached hydrogen.

H6CBP							
O202 O202′	2.818	O202	1.41	H22O	1.41	O202′	180°
O202 O102′	2.755	O202	1.34	H32O	1.43	O102′	170°
O102 O202′	2.760	O102	1.38	H12O	1.38	O202	180°
N200 N200′	3.97						
N200 N200′	3.47						
N100 N200′	3.47						
N100 N100′	3.99						
H6NBP							
O4 O2′	2.90	O4	0.88	H4O	2.05	O2′	161.4°
O4 O1′	3.67	O4	0.88	H4O	2.89	O1′	148.7°
O4 N1	3.45						
H6NBP/H6CBP							
O4 O1′	3.03	O4	1.14	H4O	1.98	O1′	151.7°
O4 O2′	3.68	O4	1.14	H4O	2.05	O2′	161.4°
O4 N1C′	2.70	O4	1.14	H4O	1.57	N1C′	170.4°
O4 N1	3.68						
O4 N1C	3.55						

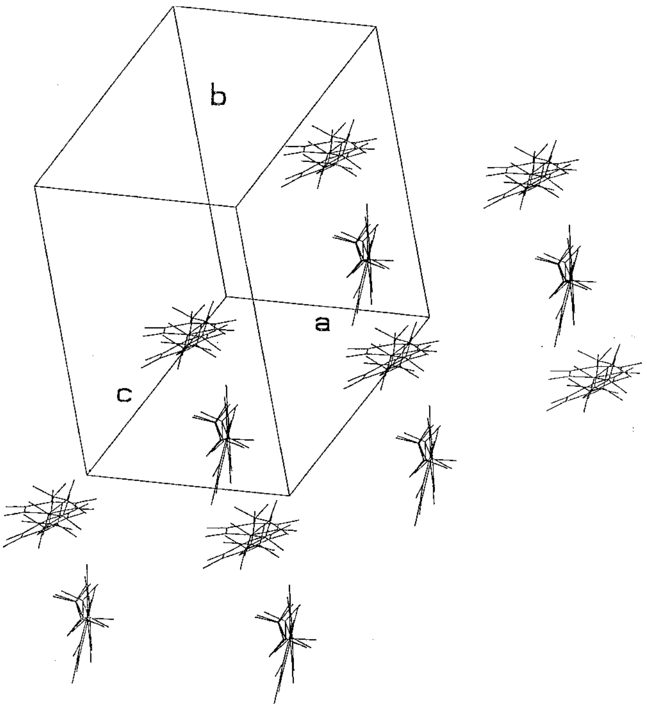


Figure 3. Projection down the long axes of the molecules of H6CBP to represent the overall packing.

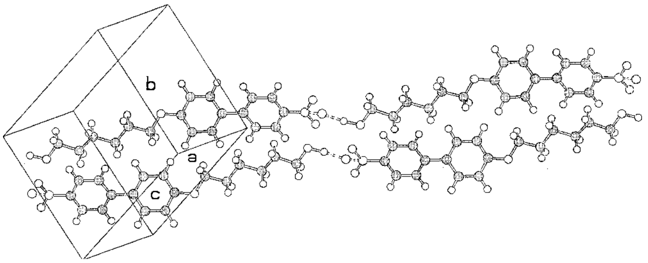


Figure 4. Representation of the head to tail interaction by dipolar forces in H6CBP/H6NCP. A similar pattern is seen in H6NCP.

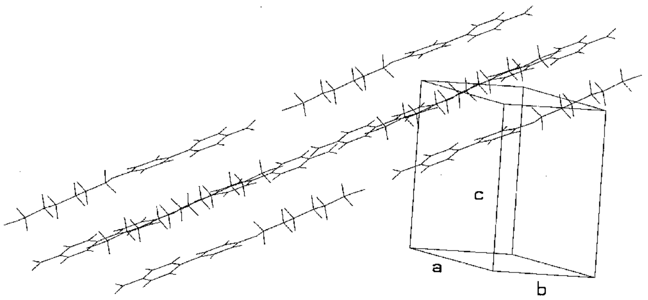


Figure 5. Representation of the sheet-like structure of H6NBP.

It should be noted that co-crystallization of similar molecules with the cyano terminal group of one compound replaced by a nitro group in the other occurs quite regularly [7] and was extensively studied for the system of shorter homologues H3CBP/H3NBP [3] of various composition.

In contrast to the lower homologues of HnCBP $n \leq 5$, hydrogen bonding does not occur between the cyano and hydroxyl groups for H6CBP, and a clear layer structure caused by the positioning of the terminal groups as for the higher homologues $n \geq 7$ does not occur either. Despite the existence of layers in the

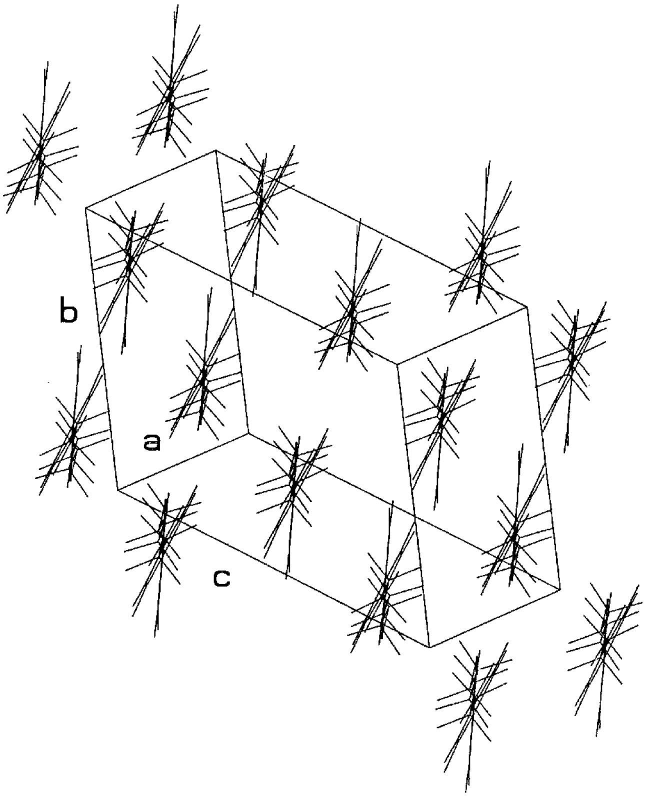


Figure 6. Projection down the long axes of the molecules of H6NBP to represent the overall packing.

crystalline state of the higher homologues, only nematic phases and not smectic phases are observed in the higher temperature range, and this holds also for the compound H6CBP. However, hydrogen bonding between the cyano and hydroxyl group was established in the crystal structure for the co-crystallized material which on the other hand is isomorphous with H6NCP.

4. Conclusion

Intermolecular interactions, especially strong polar interactions, can be easily derived from the solved crystalline structures. With the knowledge of these interactions, Raman and IR bands can be assigned to specific interactions. In the liquid crystalline state, such interactions are not available from structural X-ray investigations, but are by spectroscopic means; the bands can now be compared with those of the crystalline state and the interactions confirmed. Such a study has been performed, and the results discussed for several homologous series including the co-crystallized H3CBP/H3NBP compounds in [3]. Further, since at that time the crystal structure of H6CBP was not known, it was nevertheless predicted that hydrogen bonds occur between hydroxyl groups. This was deduced from the bands observed for the homologous series H*n*CBP.

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