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The molecular and crystal structures of a homologous series of bipolar, mesogenic biphenyls—$HO(CH_2)_nOC_6H_4.C_6H_4CN$

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The crystal and molecular structures of eight 4,4′-disubstituted biphenyls of the general formula $HO\text{–}(CH_2)_n\text{–}O\text{–}C_6H_4\text{–}C_6H_4\text{–}CN$ ($n=3$–5, 7–11) (HnCBPs) have been determined. All compounds investigated have a nearly parallel molecular arrangement in the crystalline state, with dipole–dipole interactions between the molecules. For $n \geqslant 7$, isomorphic layered structures are observed. The intermolecular packing is different for odd and even numbers of methylene units in the spacer.

1. Introduction

The investigation of the crystal structure of mesogenic compounds may provide clues for the formation and stability of liquid crystalline phases (see for example, [1–3]). Although it is not yet possible to predict the existence of a definite phase on account of the molecular shape and interactions, certain trends can be concluded by the observation of selected properties of molecules [3]. On the one hand, highly ordered smectic phases are most suitable for such a study, since they represent normally great similarities to the crystalline state [4]. On the other hand, if certain interactions or properties play an important role in the liquid crystalline as well as in the crystalline state, an investigation of the crystal structure may lead to a better understanding of the packing of molecules in the liquid crystalline phase.

For the homologous series of compounds reported in this study, the existence of a nematic phase besides the crystalline state has been proved by thermal analysis. The structure of the crystalline phase suggests strong dipole–dipole interactions which should also be present in the nematic phase.

2. Experimental, structure solution and refinement

Suitable crystals in the form of platelets of sufficient size for X-ray determination were obtained by slow evaporation of butyl acetate solutions at room temperature. Data collection was performed with a CAD 4 instrument of ENRAF NONIUS, Delft and data processing and refinement with the MolEN package. Basic crystallographic data are given in table 1.

The high R values of H4CBP may be caused by disorder in the alkyl chain not accounted for in the refinement. The crystallographic data for H6CBP with two molecules in the asymmetric unit of $P\bar{1}$ are available. The crystal structure has not yet been solved.

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Table 1. Selected crystallographic data.

	H3CBP	H4CBP	H5CBP	H6CBP	H7CBP
Formula weight/g*mol^{-1}	253·30	267·33	281·36	295·38	309·41
Radiation	Cu $K_{\alpha1}$	Cu $K_{\alpha1}$	Mo $K_{\alpha1}$	Mo $K_{\alpha1}$	Cu $K_{\alpha1}$
Space group (No. in Int. Tables)	$P2_1/n$ (14)	$P\bar{1}$ (2)	C2/c (15)	? $P\bar{1}$ (2)?	P2/a (13)
a/Å	11·921 (1)	5·644 (5)	23·896 (12)	9·75 (3)	7·106 (1)
b/Å	9·1580 (3)	9·227 (7)	9·770 (1)	13·97 (11)	6·9315 (4)
c/Å	12·845 (1)	14·403 (9)	14·013 (7)	14·24 (8)	34·861 (5)
α; β; γ/°	90; 108·198 (4); 90	107·08 (4); 94·67 (5); 89·87 (5)	90·00; 108·86 (2); 90·00	113·7 (3); 103·1 (2) 102·5 (2)	90·00; 93·255 (7); 90·0
V/Å^3	1332·16 (18)	714·4 (10)	3095·8 (23)	1626 (17)	1714·4 (4)
Number of reflections used for lattice parameter refinement	20 16° < θ < 47°	24 20° < θ < 44°	23 12° < θ < 19°	14 9° < θ < 12°	19 19° < θ < 46°
Z	4	2	8	4	4
D_c/g*cm^{-3}	1·263	1·242	1·207	1·207	1·198
μ/cm^{-1}	6·3	6·1	0·7	0·7	5·7
F(000)	536	284	1200	632	664
Number of measured reflections	1367	1778	1964	4517	1751
Number of independent reflections	873	1338	1221	3267	1274
Number of unobserved reflections ($F_o < 3\sigma$)	489	440	670	1250	477
R (R_W with $W = 1/\sigma^2$)	0·054 (0·058)	0·074 (0·105)	0·035 (0·042)		0·034 (0·043)
Scanning range	2° ≤ θ ≤ 50°	2° ≤ θ ≤ 55°	1° ≤ θ ≤ 23°	1° ≤ θ ≤ 23°	2° ≤ θ ≤ 50°

	H8CBP	H9CBP		H10CBP	H11CBP
Formula weight/g*mol^{-1}	323·44	337·46		351·49	365·52
Radiation	Cu $K_{\alpha 1}$	Mo $K_{\alpha 1}$	Cu $K_{\alpha 1}$	Cu $K_{\alpha 1}$	Cu $K_{\alpha 1}$
Space group (No. in Int. Tables)	P2/a (13)	P2/a (13)	P2/a (13)	P2/a (13)	P2/a (13)
a/Å	6·909 (1)	7·085 (6)	7·095 (4)	6·928 (4)	7·094 (3)
b/Å	7·0981 (9)	6·957 (5)	6·978 (2)	7·122 (1)	7·014 (2)
c/Å	36·883 (7)	38·43 (4)	38·46 (2)	40·60 (2)	42·095 (14)
α; β; γ/°	90·00; 91·39 (1); 90·00	90·00; 92·36 (4); 90·00	90·00; 92·38 (3); 90·00	90·00; 93·47 (2); 90·00	90·00; 92·54 (2); 90·00
V/Å^3	1808·1 (5)	1892·6 (27)	1902·3 (17)	1998·8 (14)	2092·3 (12)
Number of reflections used for lattice parameter refinement	25 $20° < \theta < 50°$	22 $9° < \theta < 18°$	16 $19° < \theta < 27°$	22 $20° < \theta < 47°$	25 $10° < \theta < 45°$
Z	4	4		4	4
D_c/g*cm^{-3}	1·188	1·178		1·168	1·160
μ/cm^{-1}	5·6	0·7		5·4	5·3
F(000)	696	728		760	792
Number of measured reflections	2039	1895		2249	2152
Number of independent reflections	1534	1109		1579	1365
Number of unobserved reflections ($F_o < 3\sigma$)	316	597		463	765
R (R_W with $W = 1/\sigma^2$)	0·044 (0·064)	0·032 (0·047)		0·038 (0·058)	0·046 (0·058)
Scanning range	$2° \leqslant \theta \leqslant 50°$	$1° \leqslant \theta \leqslant 20°$		$2° \leqslant \theta \leqslant 50°$	$2° \leqslant \theta \leqslant 50°$

3. Results and discussion

The fractional coordinates and isotropic equivalent displacement parameters B_{eq} for all compounds are listed in table 2. The crystal structure of the compound H4CBP has already been solved by Gehring *et al.* [5], with Mo-radiation. Their results, which we redetermined with Cu-radiation, agree with ours within experimental error.

3.1. *Molecular geometry and conformation*

The crystal and molecular structures of H3CBP differ significantly from all the others of the series. The molecule exhibits a conformational disorder in the alkyl chain (see figure 1). This disorder may reflect the unrealistically short distance of 1·2 Å between C(14) and C(15) and the large bond angles of more than 120° in the alkyl chain.

It is not clear at the present if a 1 : 1 mixture of the two conformational isomers exists or if a periodic transition occurs between the two conformations. Further investigations are necessary and will be carried out in the near future.

All the other compounds of the homologous series crystallize in a complete extended conformation except the terminal hydroxy groups. Figure 2 represents schematically the numbering of the atoms for the compounds H4CBP to H11CBP. The bond lengths and angles agree quite well with those of similar compounds [1, 2, 5, 6]. (Three tables of bond distances and angles are deposited in the British Library. Copies of these tables which comprise 3 pages may be obtained from the British Library, Lending Division, by quoting the number SP 16525 according to the procedure described at the end of this issue).

Surprisingly, the bond angles C(3)–C(4)–C(5) and C(12)–C(7)–C(8) deviate to some extent from the expected value of 120° for all of the structures of the series. Mandal and Paul [2] relate this phenomenon, which has been observed for other biphenyl compounds, to a strain caused by the rigidity of the biphenyl part of the molecules. It should be noted that the compound investigated by Mandal and Paul exhibits an almost coplanar arrangement of the phenyl rings. However, the compounds studied by us show dihedral angles which deviate largely from a coplanar orientation (table 3) and the deformation of the rings cannot be related to steric hindrance of the *ortho*-hydrogens.

Also the trend described by Walz *et al.* [1], that biphenylic systems tend to a coplanar arrangement of the phenyl rings with increasing length of the molecule, cannot be confirmed. An influence of the dihedral angles between the phenyl rings on the bond length C(4)–C(7) was not observed. Hence the aromatic character of this bond seems not to decrease or increase with changing dihedral angle.

3.2. *Molecular packing*

All compounds of the series are packed in an antiparallel fashion with more or less strong interactions between the polar end groups. The molecular packing may be divided into two groups. The compounds H3CBP to H5CBP exhibit an imbricated structure. Chains of single molecules or dimers are formed which are connected by terminal dipole–dipole interactions. Such molecular arrangements are often observed as solid state precursors of nematic phases [3]. The strong interactions stabilize the crystalline phase relatively well and the melting and clearing temperatures of these compounds are considerably higher than those of the analogous alkoxy- and alkyl-compounds [7–9].

From $n=7$ on, a distinct layer structure is formed which resembles strongly the molecular packing of highly ordered smectic phases. Despite this fact, only a nematic

Table 2. Positional parameters and isotropic equivalent displacement parameters B_{eq} for the investigated compounds with e.s.d.s in parentheses.

$$B_{eq}=(4/3)*[a^2*B(1,1)+b^2*B(2,2)+c^2*B(3,3)+ab(\cos\gamma)*B(1,2)+ac(\cos\beta)*B(1,3)+bc(\cos\alpha)*B(2,3)].$$

H3CBP

Atom	x	y	z	$B_{eq}/\text{Å}^2$
O(1)	−0·4014(2)	0·6263(3)	1·1453(2)	5·78(7)
O(2)	−0·3551(4)	0·5799(6)	1·4503(3)	4·6(1)
O(2X)	−0·5122(6)	0·6045(7)	1·4611(5)	9·8(2)
N(1)	0·1328(3)	0·4254(4)	0·6013(2)	5·8(1)
C(1N)	0·0676(3)	0·4429(5)	0·6501(3)	4·6(1)
C(1)	−0·0103(3)	0·4619(4)	0·7136(3)	4·0(1)
C(2)	0·0093(3)	0·3843(5)	0·8100(3)	4·5(1)
C(3)	−0·0624(3)	0·4070(4)	0·8744(3)	4·4(1)
C(4)	−0·1552(3)	0·5073(4)	0·8447(3)	3·9(1)
C(5)	−0·1752(3)	0·5818(5)	0·7463(3)	4·5(1)
C(6)	−0·1035(3)	0·5599(5)	0·6811(3)	4·6(1)
C(7)	−0·2248(3)	0·5352(4)	0·9197(3)	3·9(1)
C(8)	−0·2494(3)	0·4239(4)	0·9832(3)	4·7(1)
C(9)	−0·3101(3)	0·4490(5)	1·0572(3)	4·9(1)
C(10)	−0·3440(3)	0·5888(5)	1·0723(3)	4·6(1)
C(11)	−0·3219(3)	0·7015(5)	1·0094(3)	4·8(1)
C(12)	−0·2632(3)	0·6758(5)	0·9344(3)	4·5(1)
C(13)	−0·4272(4)	0·5137(6)	1·2103(3)	6·2(1)
C(14)	−0·4857(4)	0·5814(7)	1·2862(4)	11·0(2)
C(15)	−0·4356(7)	0·655(1)	1·3645(6)	4·8(2)
C(15X)	−0·4750(9)	0·520(1)	1·3884(7)	9·6(3)

H4CBP

O(1)	0·2092(4)	0·1835(3)	0·0051(2)	6·02(6)
O(2)	0·9040(5)	0·0982(3)	−0·3000(2)	9·02(8)
N(1)	−0·8615(6)	0·8347(4)	0·5847(2)	8·2(1)
C(1N)	−0·7482(6)	0·7635(4)	0·5262(3)	6·1(1)
C(1)	−0·6098(6)	0·6804(4)	0·4523(2)	4·97(8)
C(2)	−0·4042(6)	0·7444(4)	0·4332(2)	5·54(9)
C(3)	−0·2716(6)	0·6646(4)	0·3603(2)	5·23(9)
C(4)	−0·3335(6)	0·5164(3)	0·3037(2)	4·29(8)
C(5)	−0·5401(6)	0·4525(4)	0·3258(2)	5·04(8)
C(6)	−0·6732(6)	0·5315(4)	0·3983(2)	5·70(9)
C(7)	−0·1920(5)	0·4332(3)	0·2253(2)	4·34(8)
C(8)	−0·0410(6)	0·5064(4)	0·1810(2)	4·97(8)
C(9)	0·0935(6)	0·4287(4)	0·1073(2)	5·02(8)
C(10)	0·0866(6)	0·2726(4)	0·0762(2)	4·71(8)
C(11)	−0·0619(6)	0·1959(4)	0·1196(3)	5·73(9)
C(12)	−0·1948(6)	0·2736(4)	0·1919(2)	5·33(9)
C(13)	0·3812(6)	0·2504(4)	−0·0375(2)	5·35(9)
C(14)	0·4664(6)	0·1232(4)	−0·1198(3)	5·96(9)
C(15)	0·6514(6)	0·1727(4)	−0·1720(3)	5·88(9)
C(16)	0·7168(6)	0·0462(4)	−0·2587(2)	6·1(1)

Table 2 (*continued*).

H5CBP

Atom	x	y	z	$B_{eq}/\AA^2$
O(1)	0·31476(7)	0·0351(2)	0·4933(1)	5·25(4)
O(2)	0·14108(8)	0·0440(2)	−0·0362(1)	6·90(5)
N(1)	0·5841(1)	0·3531(2)	1·2567(2)	7·81(7)
C(1N)	0·5554(1)	0·3219(2)	1·1775(2)	5·60(7)
C(1)	0·5196(1)	0·2820(2)	1·0780(2)	4·47(6)
C(2)	0·5272(1)	0·3453(2)	0·9947(2)	4·88(6)
C(3)	0·4921(1)	0·3074(3)	0·8996(2)	4·84(6)
C(4)	0·44981(9)	0·2049(2)	0·8841(1)	3·88(5)
C(5)	0·4433(1)	0·1416(2)	0·9693(2)	4·49(6)
C(6)	0·4776(1)	0·1796(2)	1·0647(2)	4·91(6)
C(7)	0·41354(9)	0·1645(2)	0·7817(1)	3·89(5)
C(8)	0·3935(1)	0·2586(2)	0·7044(2)	4·52(6)
C(9)	0·3602(1)	0·2215(2)	0·6072(2)	4·38(6)
C(10)	0·34667(9)	0·0853(2)	0·5856(1)	4·07(6)
C(11)	0·3661(1)	−0·0113(2)	0·6615(2)	4·70(6)
C(12)	0·3983(1)	0·0279(2)	0·7574(2)	4·47(6)
C(13)	0·2941(1)	0·1275(3)	0·4111(2)	4·87(6)
C(14)	0·2585(1)	0·0475(3)	0·3207(2)	5·18(6)
C(15)	0·2365(1)	0·1318(3)	0·2254(2)	4·90(6)
C(16)	0·1993(1)	0·0501(3)	0·1361(2)	5·44(7)
C(17)	0·1807(1)	0·1252(3)	0·0386(2)	5·30(7)

H7CBP

O(1)	0·0543(2)	0·2740(2)	0·28784(4)	4·27(3)
O(2)	1·0617(2)	0·3110(2)	0·49347(4)	4·94(4)
N(1)	−0·5249(3)	0·2558(3)	−0·01217(5)	5·21(5)
C(1N)	−0·4723(3)	0·2557(3)	0·01938(6)	3·98(5)
C(1)	−0·4045(3)	0·2528(3)	0·05886(5)	3·45(5)
C(2)	−0·2984(3)	0·0978(3)	0·07273(6)	3·77(5)
C(3)	−0·2288(3)	0·0953(3)	0·11036(6)	3·51(5)
C(4)	−0·2646(3)	0·2449(3)	0·13553(5)	3·08(5)
C(5)	−0·3747(3)	0·3971(3)	0·12121(6)	3·95(5)
C(6)	−0·4444(3)	0·4028(3)	0·08350(6)	4·10(5)
C(7)	−0·1834(3)	0·2448(3)	0·17558(5)	3·01(5)
C(8)	−0·0126(3)	0·1575(3)	0·18506(5)	3·67(5)
C(9)	0·0710(3)	0·1610(3)	0·22183(6)	3·83(5)
C(10)	−0·0188(3)	0·2538(3)	0·25072(5)	3·36(5)
C(11)	−0·1928(3)	0·3366(3)	0·24239(6)	3·56(5)
C(12)	−0·2740(3)	0·3329(3)	0·20563(6)	3·49(5)
C(13)	0·2420(3)	0·2060(3)	0·29671(6)	4·13(5)
C(14)	0·3037(3)	0·2788(3)	0·33592(5)	4·13(5)
C(15)	0·4993(3)	0·2094(3)	0·34916(6)	4·00(5)
C(16)	0·5628(3)	0·2814(3)	0·38879(5)	3·89(5)
C(17)	0·7560(3)	0·2138(3)	0·40337(6)	3·97(5)
C(18)	0·8173(3)	0·2920(3)	0·44243(6)	4·05(5)
C(19)	1·0070(3)	0·2252(4)	0·45749(6)	4·58(6)

Table 2 (*continued*).

H8CBP

Atom	x	y	z	$B_{eq}/Å^2$
O(1)	0·0058(2)	0·2252(2)	0·27168(4)	3·35(3)
O(2)	0·9447(2)	0·3144(3)	0·49477(4)	4·91(4)
N(1)	−0·5238(3)	0·2418(3)	−0·01262(5)	4·33(5)
C(1N)	−0·4812(3)	0·2429(3)	0·01760(5)	3·17(5)
C(1)	−0·4223(3)	0·2476(3)	0·05524(5)	2·60(5)
C(2)	−0·3142(3)	0·3979(3)	0·06832(5)	2·79(5)
C(3)	−0·2520(3)	0·4008(3)	0·10403(5)	2·61(5)
C(4)	−0·2957(3)	0·2548(3)	0·12784(5)	2·09(4)
C(5)	−0·4087(3)	0·1064(3)	0·11430(5)	2·97(5)
C(6)	−0·4718(3)	0·1015(3)	0·07844(5)	3·24(5)
C(7)	−0·2199(3)	0·2548(3)	0·16573(5)	2·22(4)
C(8)	−0·0443(3)	0·3398(3)	0·17466(5)	2·65(5)
C(9)	0·0355(3)	0·3364(3)	0·20949(6)	2·88(5)
C(10)	−0·0628(3)	0·2453(3)	0·23665(5)	2·42(5)
C(11)	−0·2418(3)	0·1646(3)	0·22888(5)	2·61(5)
C(12)	−0·3189(3)	0·1685(3)	0·19397(5)	2·52(5)
C(13)	0·1991(3)	0·2886(3)	0·28009(6)	3·05(5)
C(14)	0·2544(3)	0·2194(3)	0·31711(6)	3·10(5)
C(15)	0·4549(3)	0·2852(3)	0·32931(5)	2·93(5)
C(16)	0·5146(3)	0·2187(3)	0·36696(6)	2·95(5)
C(17)	0·7137(3)	0·2842(3)	0·37941(5)	2·80(5)
C(18)	0·7740(3)	0·2209(3)	0·41728(5)	2·92(5)
C(19)	0·9748(3)	0·2858(3)	0·42888(6)	3·35(5)
C(20)	1·0424(3)	0·2230(4)	0·46603(6)	4·26(6)

H9CBP

O(1)	0·5803(3)	0·2743(3)	0·26000(5)	4·18(5)
O(2)	−0·5653(3)	0·3125(4)	0·49408(5)	4·87(6)
N(1)	1·0203(4)	0·2560(4)	−0·01132(6)	5·16(8)
C(1N)	0·9831(4)	0·2560(5)	0·01727(7)	3·76(8)
C(1)	0·9339(4)	0·2521(5)	0·05308(7)	3·28(8)
C(2)	0·8323(4)	0·0987(5)	0·06550(7)	3·56(8)
C(3)	0·7815(4)	0·0960(5)	0·09976(7)	3·34(8)
C(4)	0·8294(4)	0·2456(4)	0·12251(7)	2·82(7)
C(5)	0·9346(4)	0·3959(5)	0·10960(7)	3·74(8)
C(6)	0·9864(4)	0·4012(5)	0·07541(7)	4·02(8)
C(7)	0·7669(4)	0·2448(4)	0·15847(7)	2·88(7)
C(8)	0·6004(4)	0·1590(5)	0·16698(7)	3·39(8)
C(9)	0·5322(4)	0·1615(5)	0·20015(7)	3·65(8)
C(10)	0·6373(4)	0·2532(4)	0·22644(7)	3·22(7)
C(11)	0·8093(4)	0·3373(5)	0·21936(7)	3·37(8)
C(12)	0·8718(4)	0·3327(5)	0·18576(7)	3·22(7)
C(13)	0·3966(4)	0·2073(5)	0·26785(7)	3·89(8)
C(14)	0·3529(4)	0·2802(5)	0·30354(8)	3·87(8)
C(15)	0·1625(4)	0·2119(5)	0·31502(7)	3·79(8)
C(16)	0·1152(4)	0·2820(5)	0·35087(7)	3·76(8)
C(17)	−0·0720(4)	0·2123(5)	0·36328(8)	3·72(8)
C(18)	−0·1173(4)	0·2839(5)	0·39922(8)	3·87(8)
C(19)	−0·3021(4)	0·2144(5)	0·41244(8)	3·71(8)
C(20)	−0·3445(4)	0·2929(5)	0·44811(7)	4·00(8)
C(21)	−0·5277(4)	0·2267(5)	0·46148(8)	4·45(9)

Table 2 (*continued*).

H10CBP

Atom	x	y	z	$B_{eq}/Å^2$
O(1)	0·6198(2)	0·2743(2)	0·24697(3)	3·67(4)
O(2)	−0·4465(2)	0·1850(3)	0·49523(4)	5·31(5)
N(1)	1·0182(3)	0·2580(3)	−0·01154(5)	4·76(5)
C(1N)	0·9888(3)	0·2573(4)	0·01588(5)	3·61(6)
C(1)	0·9487(3)	0·2526(3)	0·05010(5)	2·95(5)
C(2)	0·8462(3)	0·1022(4)	0·06185(5)	3·21(5)
C(3)	0·8006(3)	0·0995(3)	0·09453(5)	2·89(5)
C(4)	0·8550(3)	0·2455(3)	0·11613(5)	2·45(5)
C(5)	0·9609(3)	0·3931(4)	0·10386(5)	3·28(5)
C(6)	1·0070(3)	0·3986(4)	0·07123(5)	3·51(6)
C(7)	0·7966(3)	0·2455(3)	0·15050(5)	2·56(5)
C(8)	0·6249(3)	0·1610(3)	0·15849(5)	3·12(5)
C(9)	0·5618(3)	0·1641(4)	0·19030(5)	3·25(5)
C(10)	0·6723(3)	0·2549(3)	0·21500(5)	2·75(5)
C(11)	0·8474(3)	0·3361(4)	0·20799(5)	2·96(5)
C(12)	0·9083(3)	0·3319(4)	0·17626(5)	2·92(5)
C(13)	0·4315(3)	0·2101(4)	0·25436(5)	3·32(5)
C(14)	0·3925(3)	0·2797(4)	0·28818(5)	3·38(6)
C(15)	0·1984(3)	0·2151(3)	0·29906(5)	3·22(5)
C(16)	0·1568(3)	0·2817(3)	0·33333(5)	3·22(5)
C(17)	−0·0366(3)	0·2172(3)	0·34472(5)	3·10(5)
C(18)	−0·0781(3)	0·2829(3)	0·37910(5)	3·07(5)
C(19)	−0·2707(3)	0·2166(3)	0·39049(5)	3·17(5)
C(20)	−0·3130(3)	0·2787(3)	0·42488(5)	3·28(5)
C(21)	−0·5082(3)	0·2130(4)	0·43536(5)	3·74(6)
C(22)	−0·5579(3)	0·2764(4)	0·46917(6)	4·61(7)

H11CBP

Atom	x	y	z	$B_{eq}/Å^2$
O(1)	1·4550(3)	0·2252(4)	0·26245(4)	3·99(6)
O(2)	−0·0624(3)	0·1875(4)	0·00556(5)	4·75(6)
N(1)	2·0255(4)	0·2434(5)	0·51081(6)	5·32(8)
C(1N)	1·9761(5)	0·2439(5)	0·48452(8)	3·93(9)
C(1)	1·9092(4)	0·2471(5)	0·45130(6)	3·18(8)
C(2)	1·8039(4)	0·4009(5)	0·44048(7)	3·42(8)
C(3)	1·7342(4)	0·4032(5)	0·40888(7)	3·17(8)
C(4)	1·7724(4)	0·2550(5)	0·38826(6)	2·73(8)
C(5)	1·8819(4)	0·1038(5)	0·39981(7)	3·53(8)
C(6)	1·9514(5)	0·0994(6)	0·43120(7)	3·78(8)
C(7)	1·6912(4)	0·2557(5)	0·35480(6)	2·69(8)
C(8)	1·5201(4)	0·3423(5)	0·34775(7)	3·43(8)
C(9)	1·4363(4)	0·3389(5)	0·31689(7)	3·52(8)
C(10)	1·5288(4)	0·2456(5)	0·29333(7)	2·81(7)
C(11)	1·7020(4)	0·1634(5)	0·29960(7)	3·28(8)
C(12)	1·7837(4)	0·1679(5)	0·33031(7)	3·03(8)
C(13)	1·2679(4)	0·2928(5)	0·25568(7)	3·60(8)
C(14)	1·2064(5)	0·2205(5)	0·22305(7)	3·80(8)
C(15)	1·0101(5)	0·2869(5)	0·21295(7)	3·53(8)
C(16)	0·9452(4)	0·2175(5)	0·17989(7)	3·46(8)
C(17)	0·7508(4)	0·2853(5)	0·16916(7)	3·60(8)
C(18)	0·6860(4)	0·2166(5)	0·13611(7)	3·47(8)
C(19)	0·4935(4)	0·2866(5)	0·12493(7)	3·56(8)
C(20)	0·4319(4)	0·2168(5)	0·09193(7)	3·48(8)
C(21)	0·2393(4)	0·2858(5)	0·08007(7)	3·63(8)
C(22)	0·1811(4)	0·2063(5)	0·04740(7)	3·78(9)
C(23)	−0·0110(5)	0·2729(6)	0·03540(8)	4·43(9)

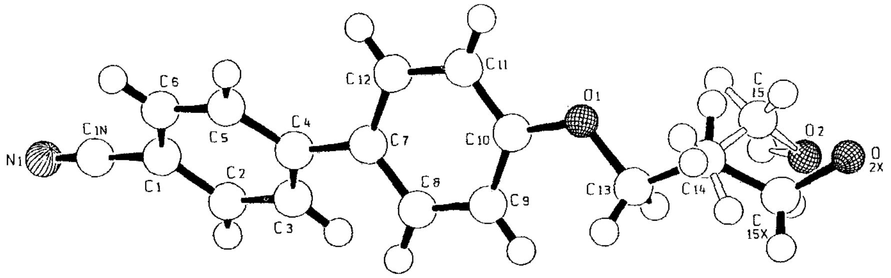


Figure 1. Molecular structure and atom labels of H3CBP.

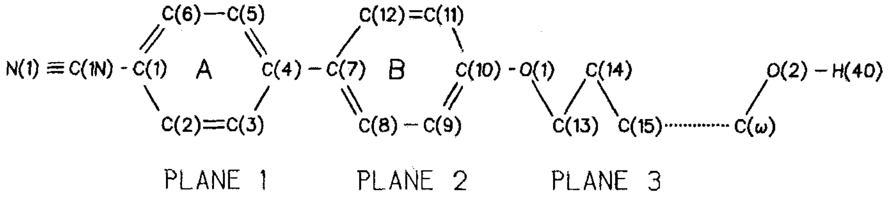


Figure 2. Schematic drawing of the molecular structure of H*n*CBP (*n* = 4, 5, 7–11) with atom labels and definition of the planes used in table 3. Plane 3 of H3CBP is defined by the atoms O(1), C(13), C(14), C(15).

Table 3. Dihedral angles (°) between the best planes (see figure 2).

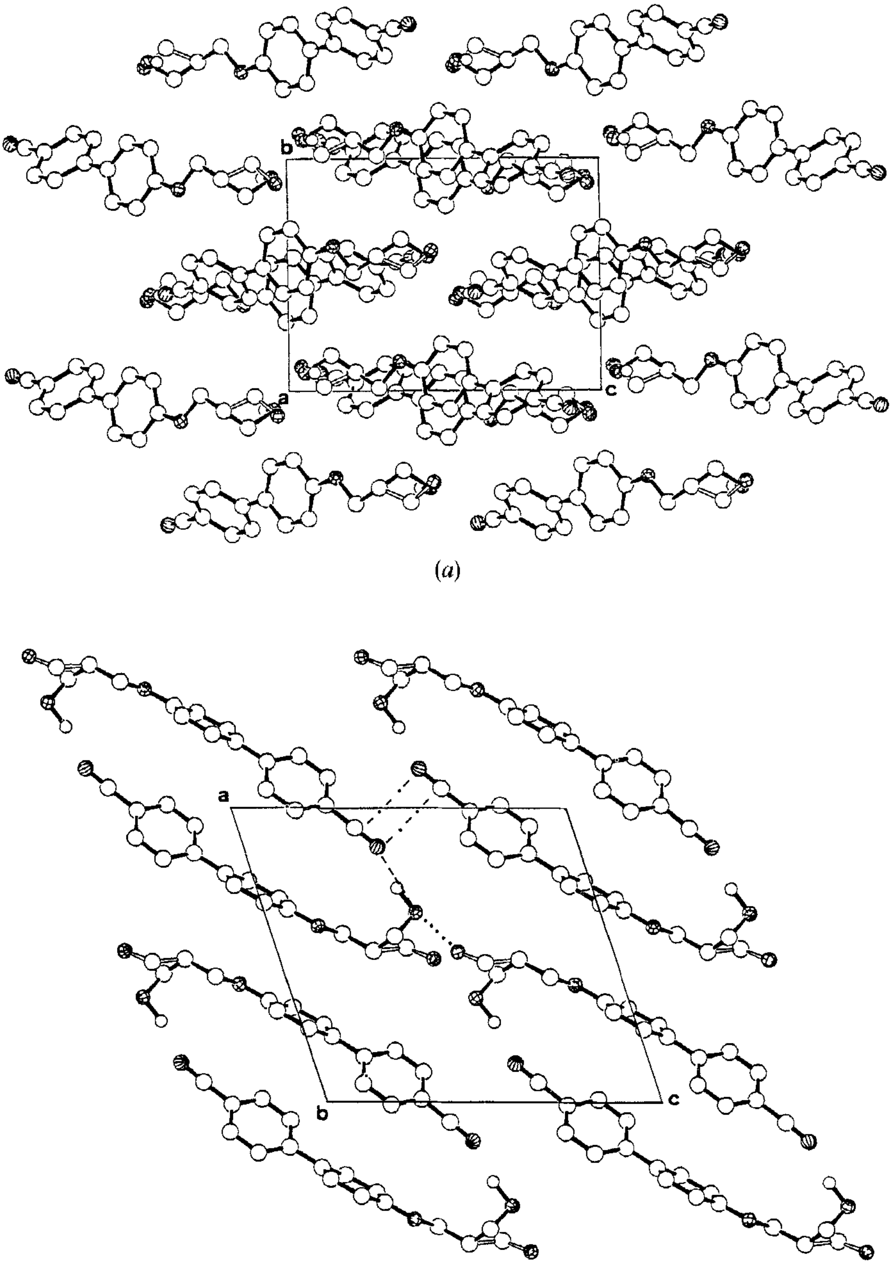
Plane No.	Plane No.	H3CBP	H4CBP	H5CBP	H7CBP
1	2	36·93(19)	22·90(23)	37·67(09)	31·35(11)
1	3	67·86(34)	12·78(80)	29·50(19)	31·82(16)
2	3	32·67(31)	12·95(60)	8·50(29)	12·86(36)

Plane No.	Plane No.	H8CBP	H9CBP	H10CBP	H11CBP
1	2	30·82(11)	31·10(17)	30·92(12)	31·14(18)
1	3	33·07(15)	31·36(21)	32·96(14)	31·84(21)
2	3	11·46(37)	12·73(47)	11·39(37)	12·08(50)

phase was observed at higher temperatures. Maybe the shape and the high stability of the crystalline phase hinders the formation of smectic phases.

The strong dipole–dipole interactions involved in the packing contacts generate a high thermal stability for the crystalline phase, and as a result, the molecular motions at the melting point are probably too high for the formation of smectic layers.

On cooling from the isotropic melt, the formation of *separate* smectic layers is hindered by dipolar repulsions of molecules lying opposite to each other, but the formation of *partially overlapping* layers recreates the structure of the crystalline phase and the dipolar attraction now obtained leads to crystallization.



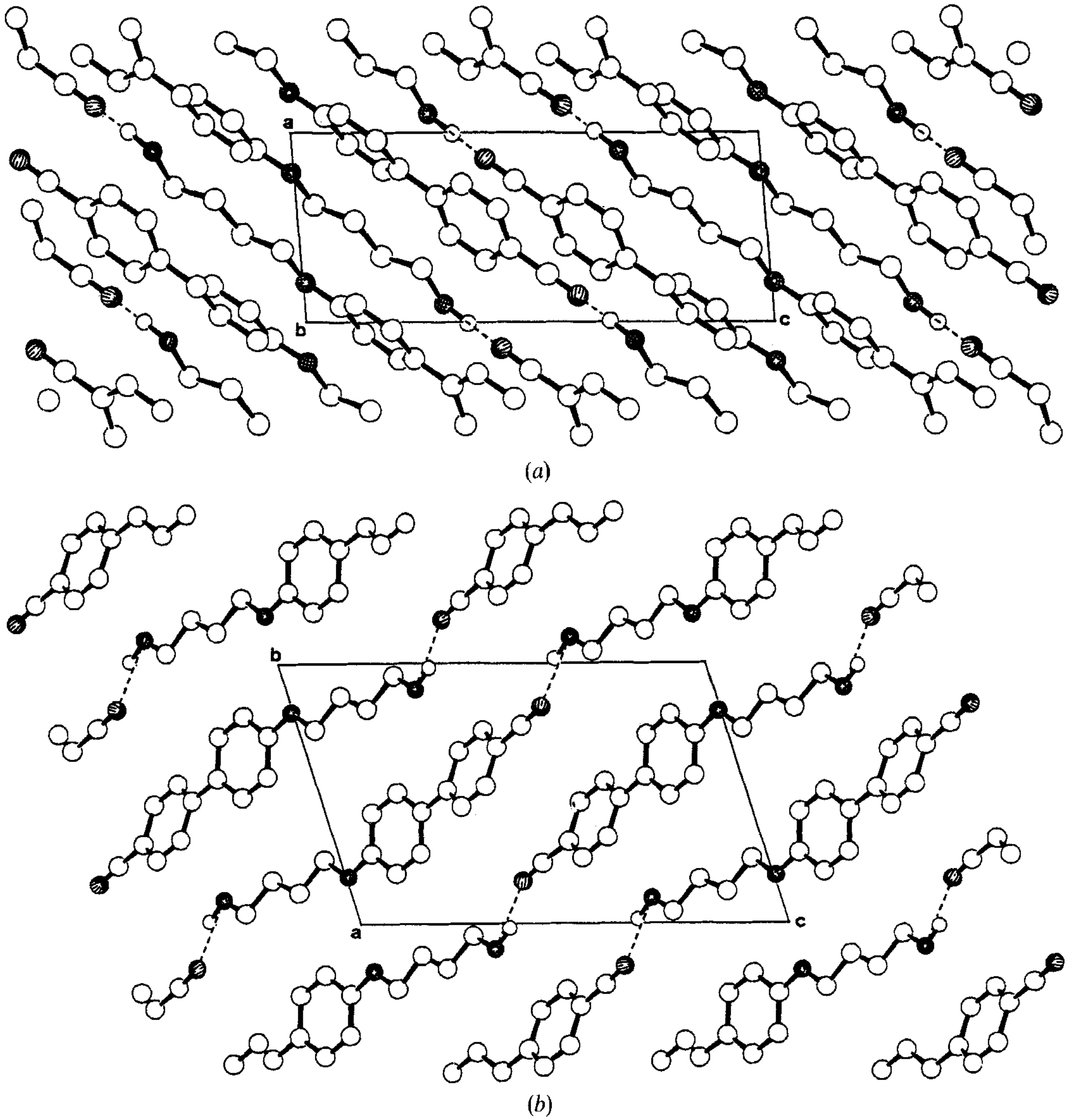
(a)

(b)

Figure 3. Molecular packing of H3CBP. (*a*) Projection on the *ac* plane. (*b*) Sheet of molecules parallel to the *ac* plane. (........), hydrogen bond between O(2) and O(2X); (- - - - - - -), hydrogen bond between O(2) and N(1); (— · — · —), dipole–dipole interaction between cyano groups.

3.2.1. *H3CBP*

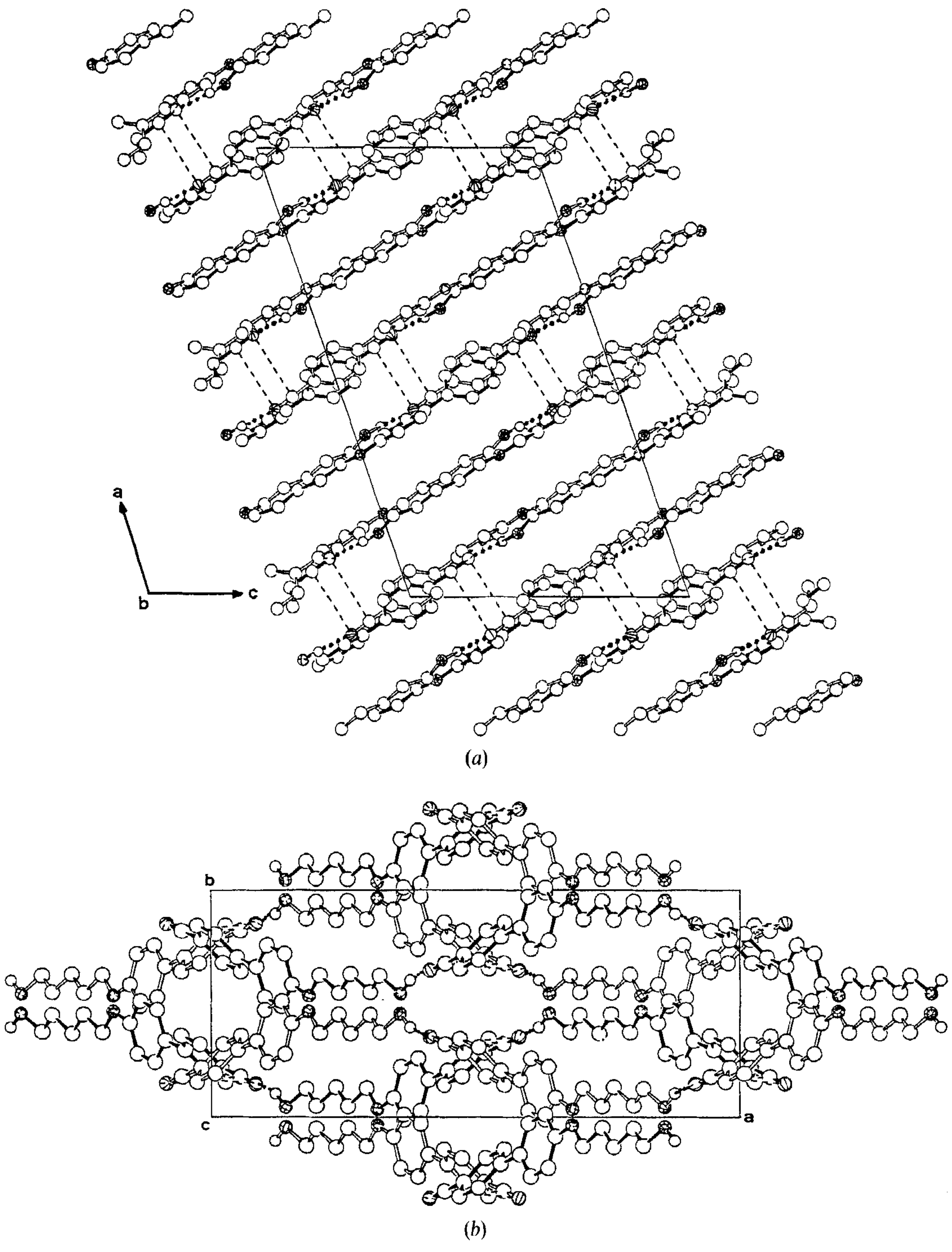
The long axes of the molecules are oriented in the [$\bar{1}01$] direction. The projection on the *bc* plane (figure 3 (*a*)) reveals layers parallel to the *ac* plane. The layers are related by a mirror glide plane along the diagonal. Two types of hydrogen bonds are detected, one between the cyano and hydroxy groups (distance between N(1) and O(2)[$-x$, $1-y$, $2-z$]$\hat{=}$2·95 Å), and the other between the hydroxy groups (distance between O(2X) and O(2)[$-1-x$, $1-y$, $3-z$]$\hat{=}$2·77 Å). The distance between the disordered oxygens O(2X) and O(2X)[$-1-x$, $1-y$, $3-z$] is at 2·14 Å unrealistically short for an intermolecular O–O contact and is related to the disordered conformation. In addition dipole–dipole interactions between cyano groups exist with a distance between N(1)



(*a*)

(*b*)

Figure 4. Molecular packing of H4CBP. (*a*) Projection on the *ac* plane. (*b*) Projection on the *bc* plane. Dashed lines represent intermolecular hydrogen bonds between cyano and hydroxy groups.



(*a*)

(*b*)

Figure 5. Molecular packing of H5CBP. (*a*) Projection on the *ac* plane. (*b*) Projection on the *ab* plane. Dashed lines represent dipole–dipole interactions between cyano groups. Dotted lines represent hydrogen bonds between cyano and hydroxy groups.

and C(1N)[$-x, 1-y, 1-z$] of 3·58 Å. A multiple melting behaviour [10] was observed which might be due to the competing interactions of the disordered structure.

3.2.2. *H4CBP*

The molecules are shifted towards each other as compared with H3CBP (cf. figure 4(*a*, *b*)), and therefore, layers cannot be defined by this kind of packing. Hydrogen bonds between terminal hydroxy and cyano groups of 2·90 Å length create chains in the [$\bar{2}$11] direction. Intermolecular distances below 4·0 Å between the cyano groups are not detected.

3.2.3. *H5CBP*

The packing of H5CBP resembles that of H4CBP with an arrangement of the molecular long axes along [103], however. The projections of the packing on the *ac* and *bc* planes are represented in figure 5. Hydrogen bonds exist between the terminal cyano and hydroxy groups with a distance between N(1) and O(2)[$0·5+x, 0·5-y, 1·5+z$] of 2·96 Å. The molecules are shifted towards each other, showing that a weak dipole–dipole interaction exists between the cyano groups (distance N(1) and C(1N)[$1-x, y, 2·5-z$] 3·75 Å) which then leads to chains of 'dimers' in the [103] direction. The possibility of 'partial bimolecular arrangements' then exists for a transition into the nematic phase as discussed by Haase *et al.* [11], for some biphenylcyclohexanes.

3.2.4. *H7CBP–H11CBP*

The compounds H7CBP to H11CBP of the series crystallize in an isomorphic layer structure as demonstrated in figures 6 and 7. Only the *c*-dimension increases with longer chain length and in *c*-direction layers of the various molecular parts can be detected. The molecular long axes point in the [301] direction.

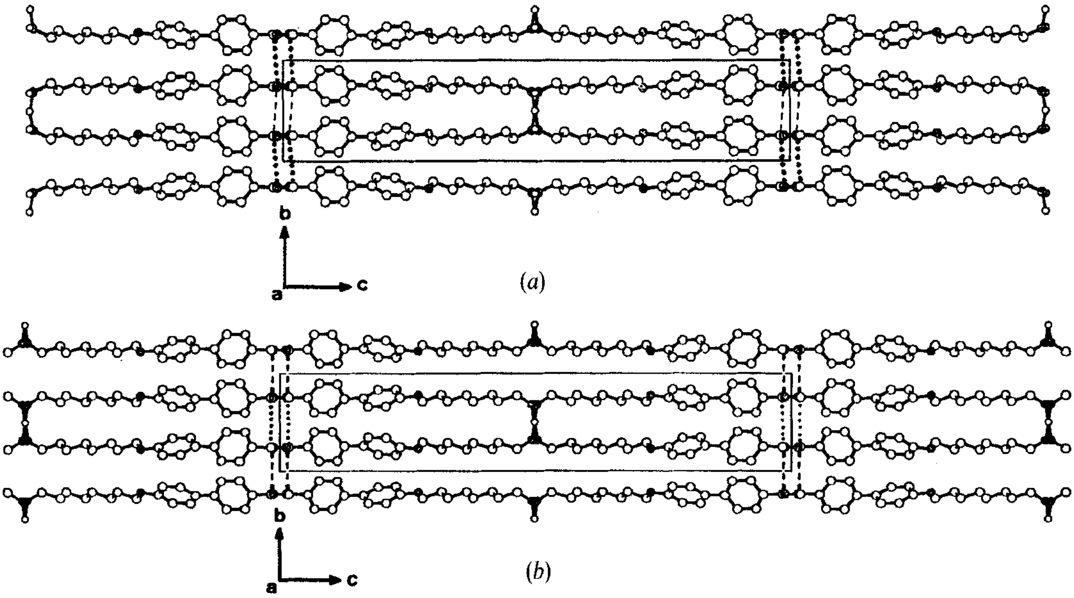


Figure 6. Comparison of dipole–dipole interactions in the molecular packing (*a*) H7CBP and (*b*) H8CBP projection on the *bc* plane. Dashed lines represent stronger and dotted lines weaker contacts.

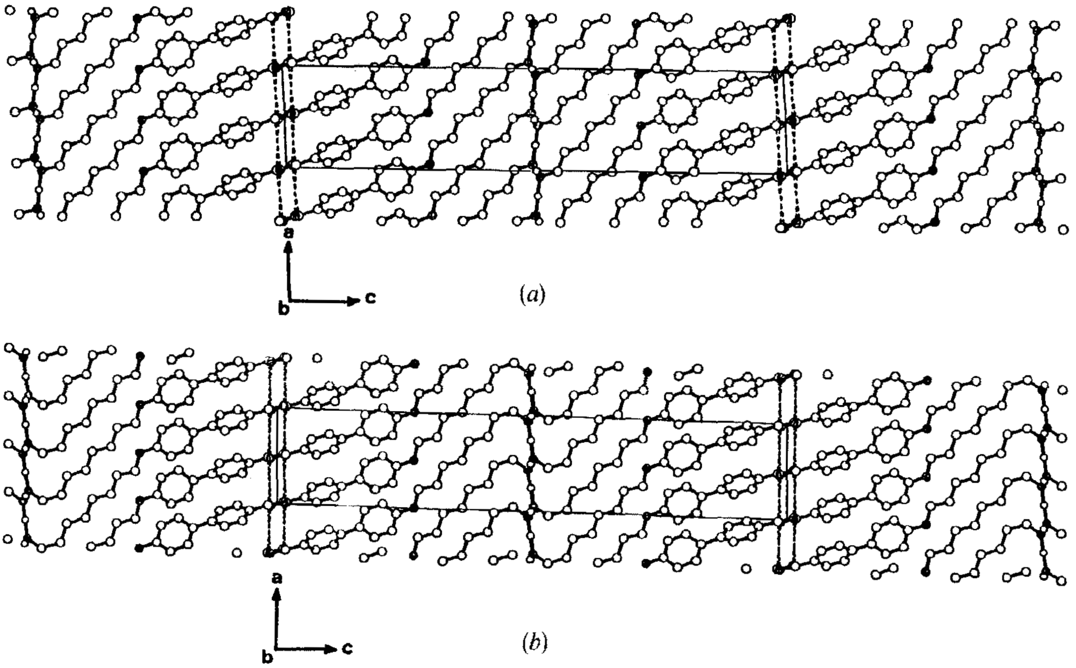


Figure 7. Projection of the molecular packing of (*a*) H7CBP and (*b*) H8CBP on the *ac* plane.

Table 4. Selected intermolecular distances (Å) for H7CBP–H11CBP.

(*a*) C(1N)–N(1) distances.

Direction	H7CBP	H8CBP	H9CBP	H10CBP	H11CBP
[100]	3·56	3·50	3·54	3·43	3·57
[$\bar{1}$00]	3·57	3·42	3·57	3·51	3·53
[010]	3·40	3·66	3·41	3·68	3·42
[0$\bar{1}$0]	3·55	3·45	3·58	3·46	3·62

(*b*) Intermolecular hydrogen bond lengths.

Direction	H7CBP	H8CBP	H9CBP	H10CBP	H11CBP
[100]	2·69	2·71	2·68	2·73	2·68
[010]	2·81	2·77	2·81	2·77	2·82

The cyano groups form layers parallel to the *ab* plane in which every cyano group is surrounded by four adjacent groups at slightly different distances (cf. table 4 (*a*)), indicating dipole–dipole interactions in all four directions. In contrast to comparable cyano compounds [2, 5], dimers are not formed; rather a network of dipolar interactions is created.

Hydrogen bonds are not formed between cyano and hydroxy groups as for lower homologues, but between the hydroxy groups themselves in the [100] direction and in the form of zig-zag lines of infinite chains (cf. table 4 (*b*)).

4. Conclusions

The dihedral angle between the two phenyl rings (table 3) changes with overall packing for the homologous series. For H3CBP to H5CBP, which crystallize in various space groups, large differences in this angle are observed. For the compounds H7CBP to H11CBP, with an isomorphic crystal structure, the angle between the two phenyl rings is almost the same, despite small differences in packing of the molecules.

An overview of the various interactions for comparable compounds of the series may lead to an interesting interpretation of the odd–even effect. The hydrogen bonds along the *b* axis point in the same direction as the shortest intermolecular C(1N)–N(1) distance for compounds with an odd number of CH_2 groups in the spacer ($n = 7, 9, 11$), but they point in the opposite direction for $n = 8$, 10 (cf. table 4). Double layers parallel to the *ac* plane, joined by strong dipolar interactions, are present for H7CBP, H9CBP and H11CBP, while all molecules are cross-linked by strong interactions in the case of H8CBP and H10CBP, leading for these compounds to higher thermal stability of the crystalline phase.

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