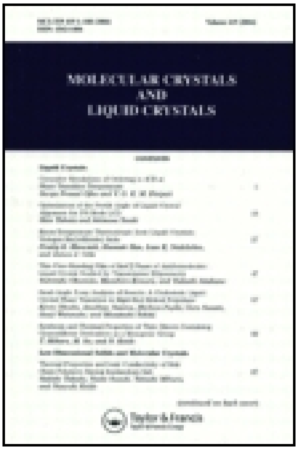

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X-ray Studies of Biphenylcyclohexanes in the Solid Crystalline and Liquid Crystalline States

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X-RAY STUDIES OF BIPHENYLCYCLOHEXANES IN THE SOLID CRYSTALLINE AND LIQUID CRYSTALLINE STATES[†]

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The crystal and molecular structures of two disubstituted biphenylcyclohexanes (BCHs) of the general formula $R—C_6H_{10}—C_6H_4—C_6H_4—X$ were determined (BCH5CN, R: C_5H_{11}, X: CN; $a = 12.671(3)$, $b = 5.567(1)$, $c = 28.695(5)$ Å, $\beta = 97.174(4)°$, space group $P2_1/c$. BCH30, R: C_3H_7, X: H, $a = 6.839(2)$, $b = 8.219(2)$, $c = 31.159(8)$ Å, $\beta = 99.63(1)°$, space group $P2_1/c$). Crystal data only is given of BCH52, R: C_5H_{11}, X: C_2H_5; $a = 17.09(2)$, $b = 6.79(1)$, $c = 37.34(3)$ Å, space group *Pbcn*. Refinement leads to $R = 0.089$ (BCH5CN) and $R = 0.128$ (BCH30) respectively. In both compounds, the molecules form layers in the crystalline state. The dihedral angles between the phenyl rings in the biphenyl unit are 2.4° (BCH5CN) and 23.8° (BCH30) respectively. X-ray examinations of the smectic states, and also of some additional BCH-compounds (BCH50, R: C_5H_{11}, X: H; BCH54, R: C_5H_{11}, X: C_4H_9; BCH7CN, R: C_7H_{15}, X: CN; BCH5NH$_2$, R: C_5H_{11}, X: NH_2) give monolayered, crystalline smectic B phases for the nonpolar compounds. The compounds containing the polar cyano-group exhibit partial bilayered structures in the smectic A phase as well as in the nematic phase. The bilayer model is discussed.

INTRODUCTION

Various liquid crystalline disubstituted biphenylcyclohexanes (BCHs) were first described by Eidenschink *et al.*[1] and Eidenschink.[2] Investigations[3,4] concerned with the densities and optical properties of the nematic phases

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[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 6–10, 1982.

as a function of temperature have recently been carried out on a number of BCHs. They also included measurements of the transition temperatures and the corresponding enthalpies, as well as studies of the magnetic properties of these compounds in the smectic and nematic states. The mesophases of the investigated substances were identified and classified by means of a polarizing microscope.[3,4]

In the smectic state, the compounds studied with nonpolar terminal groups exhibit only B-phases, whereas those compounds with polar end groups, *e.g.* cyano, show only A phases. For a structural comparison of compounds containing polar and nonpolar terminal groups, one requires a structural description of their solid crystalline and liquid crystalline states. In this respect the dihedral angles between the individual rings in a molecule and the corresponding packing arrangement in the solid crystalline state are also of special interest. Whereas the dihedral angle of + up to 42° between the phenyl rings in various biphenyls in the solid crystalline state is well known,[5] comparable structural details related to phenylcyclohexanes or biphenylcyclohexanes are unknown up till now.

EXPERIMENTAL

Substances

The biphenylcyclohexanes

$$R{-}C_6H_{10}{-}C_6H_4{-}C_6H_4{-}X$$

with

$$R = C_3H_7,\ C_5H_{11},\ C_7H_{15} \quad \text{and} \quad X = H,\ C_2H_5,\ C_4H_9,\ CN,\ NH_2$$

show nematic and smectic behavior in several cases. The transition temperatures of the compounds studied are given in Table I. These compounds

TABLE I

Transition temperatures [K] (after Ref. 3)

Abbreviations	R	X							
BCH30	C_3H_7	H	C	345	S_B	366			I
BCH50	C_5H_{11}	H	C	331	S_B	355	N	371	I
BCH52	C_5H_{11}	C_2H_5	C	308	S_B	416	N	431	I
BCH54	C_5H_{11}	C_4H_9	C	291	S_B	432	N	444	I
BCH5CN	C_5H_{11}	CN	C	368			N	494	I
BCH7CN	C_7H_{15}	CN	C	350	S_A	398	N	478	I
BCH5NH$_2$	C_5H_{11}	NH_2	C	371	S	436	N	460	I

were kindly supplied by Dr. Eidenschink, E. Merck, Darmstadt. No further purification was carried out, as the purity quoted by the manufacturer was sufficiently high and corresponds to our own observations from DSC-analysis.

Crystal data

Crystals for X-ray examinations were obtained by slow evaporation of a methanolic solution of the compound. Suitable crystals for X-ray analysis were mounted on a goniometer head. Their lattice dimensions were determined by a least-squares refinement of the setting angles for a number of strong reflections (BCH5CN: 50; BCH30: 41; BCH52: 28) on an automatic STOE-4-circle-diffractometer with MoK_α-radiation. The selected space groups are based on the reflections which are systematically absent. The crystal data for the three compounds investigated are given in Table II.

The reflection intensities for the structural determination of BCH5CN and BCH30 were measured with the STOE-4-circle-diffractometer with MoK_α-radiation. For data concerning the longer c-axis of BCH52, the examination has to be carried out with CuK_α-radiation. This investigation is under way.

The reflection intensities for both compounds were very weak owing to the relatively low melting points of the substances in question. For BCH5CN, a second data collection procedure with a crystal of dimensions $a \times b \times c \sim 1 \times 4 \times 0.5$ mm was necessary. The original data were based on 1875 reflections of which only ~1000 were greater than 2σ (F).

TABLE II

Crystal data

	BCH5CN	BCH30	BCH52
Molecular formula	$C_{24}H_{29}N$	$C_{21}H_{26}$	$C_{25}H_{34}$
Formula weight [g/mol]	331.50	278.44	334.55
Space group	$P2_1/c$	$P2_1/c$	$Pbcn$
a [Å]	12.671(3)	6.839(2)	17.09(2)
b [Å]	5.567(1)	8.219(2)	6.79(1)
c [Å]	28.695(5)	31.159(8)	37.34(3)
β [°]	97.174(4)	99.63(1)	
V_c [Å^3]	2008.3	1726.8	4333
D_c [g · cm^{-3}]	1.12	1.07	1.03
Z	4	4	8
Independent reflections	2649	2267	
μ (MoK_α)	0.31	0.29	

Structure determination and refinement

The structure of BCH5CN was solved by direct methods (SHELX) based on the first collected intensity set. The refinement ended at $R = 0.18$. Because of the low intensity of this first set, the intensity set collected using a second crystal was used for further refinement. This crystal was mounted along the prismatic *b*-axis. Owing to its dimensions, the entire crystal was not exposed to the X-ray beam. Accordingly a correction was made to compensate for this. In addition Lorentz and polarization corrections were performed.

The anisotropic refinement with 2093 nonzero reflections of all but the hydrogen atoms leads to an *R*-value of 0.15. At this stage, the hydrogen positions were calculated using a C—H bond length of 0.96 Å. These positions were introduced into the refinement procedure though only as dependent parameters in connection with the appropriate carbon atoms. This refinement leads to $R = 0.099$ ($R_W = 0.084$).

The difference map shows maxima in the surroundings of the alkyl chain. Thus the four strongest peaks of this map were interpreted as disordered C-atoms. These positions were weighted with 20% of a carbon atom and the original atomic positions of the alkyl chain analogously with 80%. With this refinement, the *R*-value converged at 0.083 ($R_W = 0.067$). The difference map at this stage shows maxima lower than 0.2 electron/$Å^3$ and so, the refinement was terminated. The resultant atomic coordinates are given in Table III.*

In solving the structure of BCH30 with direct methods (using 1420 nonzero reflections), all the calculated *E*-maps show interconnected triangles which are often present in hexagonal structures. The correct solution was obtained by starting with an eight atom fragment applying a Fourier synthesis. As a result of this, the three rings and the first carbon atom of the propyl chain were obtained. The remaining two carbon atoms were extracted from further Fourier synthesis. The least-squares refinement with anisotropic temperature factors results in $R = 0.17$. Introducing the hydrogen atoms calculated from the molecular geometry, the refinement converged at $R = 0.128$ and $R_W = 0.088$. The atomic coordinates are given in Table IV.*

X-ray investigations of the liquid crystalline phases

For the X-ray examinations of the liquid crystalline states the samples were introduced into Lindemann glass capillaries with a diameter of 0.7 mm. An

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*A list of observed and calculated structure factors is available from the authors on request.

TABLE III

Atomic parameters for BCH5CN

Name	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	.0211	−0.348	.2852	.1205	.1365	.1285	.0142	.0578	.0014
	.0003	.0006	.0001	.0026	.0026	.0025	.0023	.0023	.0021
C(1)	.0935	−.0298	.2654	.0995	.0964	.0953	.0135	.0286	.0074
	.0003	.0006	.0001	.0028	.0027	.0027	.0024	.0023	.0022
C(2)	.1861	−.0244	.2413	.0864	.0830	.0748	.0079	.0181	.0097
	.0002	.0005	.0001	.0022	.0022	.0020	.0020	.0018	.0018
C(3)	.2061	−.2013	.2106	.0867	.1066	.0945	−.0153	.0227	−.0165
	.0003	.0006	.0001	.0025	.0029	.0026	.0022	.0022	.0023
H(3)	.1555	−.3292	.2046	.1035^{x}					
	.0003	.0006	.0001	.0000					
C(4)	.2977	−.1933	.1894	.0904	.1006	.0906	−.0104	.0251	−.0261
	.0003	.0006	.0001	.0025	.0028	.0025	.0023	.0022	.0021
H(4)	.3111	−.3205	.1683	.1010					
	.0003	.0006	.0001	.0000					
C(5)	.3713	−.0131	.1965	.0771	.0619	.0611	.0017	.0054	.0036
	.0002	.0005	.0001	.0021	.0020	.0019	.0019	.0016	.0016
C(6)	.3490	.1613	.2277	.1194	.0783	.1213	−.0137	.0449	−.0270
	.0003	.0005	.0001	.0029	.0023	.0029	.0022	.0024	.0021
H(6)	.3978	.2928	.2336	.1129					
	.0003	.0005	.0001	.0000					
C(7)	.2585	.1551	.2495	.1354	.0926	.1249	.0075	.0629	−.0199
	.0003	.0006	.0001	.0032	.0025	.0029	.0024	.0026	.0023
H(7)	.2449	.2832	.2703	.1236					
	.0003	.0006	.0001	.0000					
C(8)	.4687	−.0069	.1728	.0705	.0609	.0670	.0023	.0029	.0015
	.0002	.0006	.0001	.0020	.0021	.0020	.0019	.0016	.0018
C(9)	.4897	−.1767	.1402	.0908	.0752	.1301	−.0211	.0390	−.0336
	.0003	.0006	.0001	.0026	.0024	.0030	.0020	.0024	.0024
H(9)	.4395	−.3039	.1323	.1050					
	.0003	.0006	.0001	.0000					
C(10)	.5800	−.1671	.1181	.0968	.0774	.1272	−.0107	.0413	−.0331
	.0003	.0006	.0001	.0027	.0026	.0031	.0023	.0025	.0022
H(10)	.5910	−.2937	.0965	.1067					
	.0003	.0006	.0001	.0000					
C(11)	.6546	.0070	.1261	.0769	.0660	.0795	−.0050	.0094	−.0064
	.0002	.0006	.0001	.0023	.0024	.0023	.0021	.0019	.0020
C(12)	.6336	.1761	.1585	.0922	.1012	.1139	−.0344	.0265	−.0311
	.0003	.0006	.0001	.0028	.0028	.0030	.0023	.0024	.0025
H(12)	.6846	.3013	.1667	.1102					
	.0003	.0006	.0001	.0000					
C(13)	.5445	.1684	.1814	.1070	.0915	.0993	−.0215	.0269	−.0368
	.0003	.0006	.0001	.0029	.0027	.0028	.0025	.0024	.0021
H(13)	.5330	.2939	.2031	.1067					
	.0003	.0006	.0001	.0000					
C(14)	.7527	.0159	.1024	.0814	.0786	.0958	−.0080	.0202	−.0104
	.0002	.0006	.0001	.0022	.0025	.0024	.0021	.0020	.0021
H(14)	.7461	−.1049	.0783	.0920					
	.0002	.0006	.0001	.0000					
C(15)	.7662	.2534	.0781	.1019	.1234	.1209	.0036	.0355	.0267
	.0003	.0007	.0001	.0028	.0032	.0030	.0024	.0025	.0025

TABLE III *(continued)*

Name	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H(15A)	.7061	.2829	.0549	.1237					
	.0003	.0007	.0001	.0000					
H(15B)	.7694	.3749	.1019	.1237					
	.0003	.0007	.0001	.0000					
C(16)	.8681	.2637	.0553	.1173	.1218	.1316	−.0146	.0386	.0134
	.0003	.0007	.0001	.0033	.0031	.0035	.0027	.0031	.0026
H(16A)	.8641	.1441	.0311	.1324					
	.0003	.0007	.0001	.0000					
H(16B)	.8750	.4198	.0418	.1324					
	.0003	.0007	.0001	.0000					
C(17)	.9640	.2171	.0880	.0947	.1271	.1108	−.0330	.0393	−.0275
	.0003	.0006	.0001	.0027	.0030	.0029	.0025	.0025	.0024
H(17)	.9679	.3316	.1132	.1184					
	.0003	.0006	.0001	.0000					
C(18)	.9532	−.0268	.1115	.0819	.1611	.1257	.0139	.0188	.0093
	.0002	.0006	.0001	.0025	.0034	.0030	.0026	.0023	.0026
H(18A)	.9487	−.1475	.0875	.1335					
	.0002	.0006	.0001	.0000					
H(18B)	1.0147	−.0561	.1339	.1335					
	.0002	.0006	.0001	.0000					
C(19)	.8511	−.0482	.1344	.0828	.1178	.1255	.0033	.0228	.0198
	.0002	.0006	.0001	.0023	.0028	.0028	.0022	.0022	.0023
H(19A)	.8570	.0709	.1588	.1175					
	.0002	.0006	.0001	.0000					
H(19B)	.8439	−.2042	.1479	.1175					
	.0002	.0006	.0001	.0000					
C(20)†	1.0626	.2571	.0637	.0900	.1261	.1030	.0095	.0211	.0134
	.0003	.0010	.0001	.0037	.0043	.0038	.0032	.0032	.0031
H(20A)	1.0682	.1170	.0447	.1151					
	.0003	.0010	.0001	.0000					
H(20B)	1.0562	.3973	.0441	.1151					
	.0003	.0010	.0001	.0000					
C(21)†	1.1544	.2819	.0896	.0821	.4368	.2972	−.0940	.0734	−.1335
	.0007	.0023	.0003	.0053	.0134	.0140	.0073	.0080	.0104
H(21A)	1.1677	.1265	.1035	.2925					
	.0007	.0023	.0003	.0000					
H(21B)	1.1391	.3944	.1132	.2925					
	.0007	.0023	.0003	.0000					
C(22)†	1.2710	.3354	.0748	.2262	.3141	.1243	−.0522	−.0324	−.0471
	.0009	.0024	.0003	.0103	.0104	.0102	.0084	.0085	.0092
H(22A)	1.2615	.4963	.0629	.2467					
	.0009	.0024	.0003	.0000					
H(22B)	1.3266	.3332	.1007	.2467					
	.0009	.0024	.0003	.0000					
C(23)†	1.2974	.2063	.0429	.1457	.1717	.1118	.0219	.0209	−.0312
	.0005	.0012	.0003	.0053	.0059	.0054	.0053	.0041	.0043
H(23A)	1.2456	.2205	.0155	.1555					
	.0005	.0012	.0003	.0000					
H(23B)	1.3006	.0425	.0534	.1555					
	.0005	.0012	.0003	.0000					
C(24)	1.4085	.2899	.0304	.1081	.2977	.1516	−.0049	.0488	.0129
	.0003	.0009	.0001	.0033	.0057	.0038	.0041	.0031	.0042

TABLE III *(continued)*

Name	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H(24A)	1.4278	.1875	.0059	.1999					
	.0003	.0009	.0001	.0000					
H(24B)	1.4057	.4535	.0197	.1999					
	.0003	.0009	.0001	.0000					
H(24C)	1.4606	.2755	.0576	.1999					
	.0003	.0009	.0001	.0000					
C(20)′[††]	1.0940	.1123	.0789	.0825					
	.0018	.0032	.0007	.0006					
C(21)′[††]	1.1689	.2782	.1030	.0769					
	.0027	.0039	.0010	.0006					
C(22)′[††]	1.2663	.3461	.0861	.0776					
	.0023	.0048	.0012	.0006					
C(23)′[††]	1.2449	.3753	.0415	.0883					
	.0015	.0044	.0009	.0006					

[*] The U_{iso} of the hydrogens are given without standard deviations.
[†] Occupation factor 0.8.
[††] Occupation factor 0.2.

TABLE IV

Atomic parameters for BCH30

Name	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(2)	−.1753	.4143	.1404	.1574	.1270	.0886	−.0195	−.0415	−.0014
	.0012	.0011	.0002	.0084	.0082	.0057	.0072	.0061	.0072
H(2)	−.2777	.4105	.1153	.1731[*]					
	.0012	.0011	.0002	.0000					
C(3)	−.2091	.4702	.1763	.0878	.1485	.1119	.0126	−.0222	.0003
	.0012	.0012	.0003	.0063	.0100	.0068	.0063	.0063	.0075
H(3)	−.3378	.5146	.1776	.0966					
	.0012	.0012	.0003	.0000					
C(4)	−.0682	.4634	.2133	.0802	.1139	.1183	.0062	.0104	.0073
	.0010	.0009	.0002	.0056	.0074	.0059	.0055	.0049	.0059
H(4)	−.1036	.5035	.2399	.0882					
	.0010	.0009	.0002	.0000					
C(5)	.1193	.4080	.2148	.0789	.0918	.0427	−.0042	.0193	−.0031
	.0011	.0010	.0002	.0066	.0069	.0046	.0056	.0045	.0049
C(6)	.1504	.3523	.1767	.0887	.1079	.1002	.0128	−.0093	.0001
	.0011	.0010	.0003	.0066	.0079	.0061	.0055	.0060	.0060
H(6)	.2763	.3019	.1758	.0975					
	.0011	.0010	.0003	.0000					
C(7)	.0146	.3564	.1379	.1665	.1078	.1161	−.0243	−.0262	.0087
	.0016	.0012	.0003	.0104	.0095	.0082	.0088	.0087	.0065
H(7)	.0503	.3259	.1105	.1831					
	.0016	.0012	.0003	.0000					
C(8)	.2722	.4030	.2530	.0707	.0555	.0862	−.0060	.0017	−.0006
	.0011	.0010	.0002	.0059	.0062	.0060	.0053	.0050	.0053
C(9)	.2625	.5061	.2891	.0659	.0692	.1214	.0066	−.0072	.0105
	.0010	.0009	.0003	.0055	.0067	.0066	.0049	.0053	.0058

TABLE IV *(continued)*

Name	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H(9)	.1535	.5810	.2868	.0724					
	.0010	.0009	.0003	.0000					
C(10)	.4003	.5015	.3270	.0729	.0909	.0724	.0161	.0161	−.0514
	.0011	.0009	.0002	.0053	.0069	.0053	.0052	.0044	.0048
H(10)	.3899	.5736	.3507	.0802					
	.0011	.0009	.0002	.0000					
C(11)	.5572	.3946	.3310	.0644	.0695	.0933	.0078	.0107	.0047
	.0010	.0010	.0002	.0054	.0060	.0056	.0051	.0043	.0054
C(12)	.5735	.2963	.2947	.0917	.1113	.1030	.0336	.0030	−.0188
	.0011	.0010	.0002	.0061	.0079	.0059	.0058	.0056	.0063
H(12)	.6880	.2277	.2962	.1009					
	.0011	.0010	.0002	.0000					
C(13)	.4281	.2962	.2579	.0868	.0949	.0661	.0286	.0122	−.0141
	.0011	.0010	.0002	.0060	.0073	.0050	.0056	.0045	.0048
H(13)	.4365	.2196	.2350	.0955					
	.0011	.0010	.0002	.0000					
C(14)	.7031	.3910	.3735	.0804	.1004	.0594	.0138	.0052	−.0061
	.0010	.0010	.0002	.0056	.0067	.0044	.0058	.0038	.0051
H(14)	.6905	.4867	.3905	.0885					
	.0010	.0010	.0002	.0000					
C(15)	.6711	.2455	.4001	.0962	.1383	.0714	−.0030	.0085	.0130
	.0010	.0011	.0002	.0063	.0081	.0050	.0062	.0046	.0059
H(15A)	.6924	.1485	.3843	.1059					
	.0010	.0011	.0002	.0000					
H(15B)	.5365	.2478	.4052	.1059					
	.0010	.0011	.0002	.0000					
C(16)	.8155	.2486	.4431	.1542	.1270	.1022	.0035	−.0216	.0244
	.0013	.0012	.0002	.0092	.0082	.0070	.0082	.0072	.0065
H(16A)	.7829	.3412	.4593	.1696					
	.0013	.0012	.0002	.0000					
H(16B)	.8002	.1510	.4592	.1696					
	.0013	.0012	.0002	.0000					
C(17)	1.0226	.2565	.4418	.0930	.1869	.0760	.0453	−.0102	−.0199
	.0013	.0014	.0002	.0073	.0111	.0063	.0083	.0059	.0067
H(17)	1.0725	.1718	.4253	.1023					
	.0013	.0014	.0002	.0000					
C(18)	1.0551	.3946	.4132	.0668	.2328	.0923	−.0148	−.0040	−.0190
	.0011	.0013	.0002	.0058	.0123	.0065	.0076	.0051	.0078
H(18A)	1.1919	.4006	.4098	.0735					
	.0011	.0013	.0002	.0000					
H(18B)	1.0198	.4910	.4275	.0735					
	.0011	.0013	.0002	.0000					
C(19)	.9188	.3942	.3677	.1021	.1332	.1259	.0007	−.0149	.0001
	.0012	.0011	.0002	.0065	.0079	.0069	.0071	.0057	.0067
H(19A)	.9407	.4859	.3500	.1123					
	.0012	.0011	.0002	.0000					
H(19B)	.9464	.2956	.3534	.1123					
	.0012	.0011	.0002	.0000					
C(20)	1.1600	.2727	.4849	.1524	.1962	.1874	.0895	−.0934	−.1086
	.0012	.0014	.0003	.0103	.0117	.0102	.0091	.0086	.0091

TABLE IV *(continued)*

Name	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H(20A)	1.1435	.3753	.4985	.1677					
	.0012	.0014	.0003	.0000					
H(20B)	1.1038	.1878	.5001	.1677					
	.0012	.0014	.0003	.0000					
C(21)	1.3210	.2201	.4943	.2289	.3201	.1096	.1456	−.0871	−.0707
	.0014	.0017	.0003	.0140	.0169	.0076	.0132	.0091	.0095
H(21A)	1.3763	.3057	.4792	.2518					
	.0014	.0017	.0003	.0000					
H(21B)	1.3364	.1180	.4803	.2518					
	.0014	.0017	.0003	.0000					
C(22)	1.4475	.2243	.5388	.1910	.1779	.1223	.0483	−.0610	−.0079
	.0011	.0011	.0002	.0093	.0096	.0069	.0084	.0070	.0077
H(22A)	1.5848	.2035	.5378	.2101					
	.0011	.0011	.0002	.0000					
H(22B)	1.4354	.3260	.5533	.2101					
	.0011	.0011	.0002	.0000					
H(22C)	1.3955	.1383	.5545	.2101					
	.0011	.0011	.0002	.0000					

[a] The U_{iso} of the hydrogens are given without standard derivation.

oven, specially constructed for X-ray investigations, allowed temperature dependent measurements to be made in the range of 300 K–570 K with an accuracy of ±1 K. For the exposure, nickel-filtered CuK_α-radiation perpendicular to the glass carpillary was used. The camera used was of the flat-plate type. The distance between sample and film was 60 mm. Calibration was performed with aluminium powder.

The more or less complete orientation of the liquid crystalline sample in the capillary tube is dependent on the orientational forces of the surface. One can practically attain total orientation if this sample is slowly cooled from the isotropic phase in the presence of a magnetic field of the magnitude of 1.2 T. Owing to the instability of $BCH5NH_2$ in the isotropic state, orientation commencing with the isotropic phase was not possible.

A cooling rate of 0.5 K/min was employed throughout the temperature range, except in the regions of phase transitions, where the cooling process was halted for 30 min. The X-ray exposures were preceded by the abovementioned orientating procedure and thereafter commenced at the lowest temperature of the smectic or nematic phase. The temperature of the samples was subsequently raised with a rate of 0.5 K/min in steps of 2–3 K. The aim of this was to obtain an insight into the temperature dependence of the distances between the molecules or the layers.

The X-ray patterns of the liquid crystalline samples were evaluated with a Joyce MKIIIC-microdensitometer.

RESULTS AND DISCUSSION

Molecular structures

In Figures 1 and 2 the respective molecular structures of BCH5CN and BCH30 are presented. It can be shown that the molecules are arranged in such a manner that an imaginary line through their longest extension is nearly parallel to the axis through the biphenyl rings. In Figure 2, the chair-conformation of the cyclohexyl ring is clearly indicated, as well as the disubstitution at the equatorial position of carbon atoms C(14) and C(17) of the cyclohexyl unit.

Further to this, the subsequent alkyl groups possess a gauche conformation up to carbon atom C(22) . This is immediately followed by a kink (between C(22) and C(23)) in the conformation of BCH5CN. This may be related to the packing arrangement in the crystalline state, in the sense that the fully extended gauche conformation is hindered by the rod-like packing in the crystalline state. Nevertheless it should be mentioned that the thermal vibrations of the carbon atoms of the alkyl groups are appreciable. As already discussed in the experimental section, some evidence exists for a partial occupancy of more than one lattice place per atom. It might be

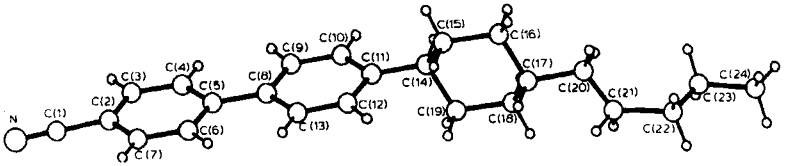

FIGURE 1 BCH5CN molecule.

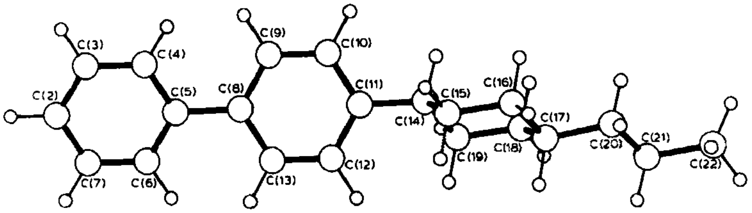

FIGURE 2 BCH30 molecule.

mentioned that the somewhat shorter or longer carbon-carbon distances in Table V may be due to this partial occupancy. The remaining bond lengths and bond angles (not included in the table) are normal within the limits of error.

In Table VI the dihedral angles between the whole rings are presented. It is shown that there is a noteworthy difference between the dihedral angles of the two phenyl rings in each molecule. Whereas the biphenyl group in BCH5CN is virtually coplanar (dihedral angle = 2.4°), this group is twisted by 23.8° in BCH30. We interpret this difference in terms of the different packing in the crystalline state. For comparison, an angle of 35° has been reported for isobutyl 4-[4′-phenylbenzylideneamino]cinnamate,[6] and 4.4′-disubstituted biphenyls show angles of up to 42°.[5]

TABLE V

Bond distances with their e.s.d's

	BCH5CN	BCH30
N(1)—C(1)	1.139(5)	
C(1)—C(2)	1.434(5)	
C(2)—C(3)	1.366(4)	1.266(12)[*]
C(3)—C(4)	1.374(4)	1.373(10)
C(4)—C(5)	1.368(5)	1.355(11)
C(5)—C(6)	1.374(4)	1.321(12)
C(6)—C(7)	1.373(4)	1.397(13)
C(7)—C(2)	1.357(5)	1.397(14)
C(5)—C(8)	1.481(4)	1.448(10)
C(8)—C(9)	1.380(5)	1.419(12)
C(9)—C(10)	1.377(5)	1.383(10)
C(10)—C(11)	1.353(5)	1.376(11)
C(11)—C(12)	1.373(5)	1.409(12)
C(12)—C(13)	1.375(5)	1.386(11)
C(13)—C(8)	1.371(5)	1.370(11)
C(11)—C(14)	1.491(4)	1.520(9)
C(14)—C(15)	1.514(5)	1.492(11)
C(15)—C(16)	1.520(4)	1.527(10)
C(16)—C(17)	1.462(6)	1.426(12)
C(17)—C(18)	1.530(5)	1.482(14)
C(18)—C(19)	1.527(4)	1.560(10)
C(19)—C(14)	1.497(4)	1.516(10)
C(17)—C(20)	1.522(5)	1.511(11)
C(20)—C(21)	1.306(10)[*]	1.173(11)[*]
C(21)—C(22)	1.615(14)[*]	1.507(11)
C(22)—C(23)	1.242(11)[*]	
C(23)—C(24)	1.567(7)	
C(20)′—C(21)′	1.438(38)	
C(21)′—C(22)′	1.432(43)	
C(22)′—C(23)′	1.285(41)[*]	

[*] Anomalous values (see text).

TABLE VI

Dihedral angles

	BCH5CN	BCH30
1–2	2.4	23.8
1–3	79.4	54.4
2–3	81.7	75.8

Plane 1: C(2) to C(7) (Phenyl ring A); Plane 2: C(8) to C(13) (Phenyl ring B); Plane 3: C(15), C(16), C(18), C(19) (Cyclohexyl).

Molecular packing

The molecular arrangement of crystalline BCH5CN is shown in Figure 3. The molecules are extended parallel, lying perpendicular to [010], with $y \sim 0$ and $y \sim 0.5$ in a head-to-tail configuration. The normal to the biphenyl rings form an angle of approximately 57° with their projection in the (010)-plane. The projection of the long molecular axis in the (010)-plane forms an angle of approximately 55° with the *c*-axis. The alternating head-to-tail arrangement results in a stack formation along the *b*-axis so that the plane of phenyl ring *A* of one molecule forms an angle of approximately 66° with the plane of phenyl ring *B* of the next molecule and *vice versa*. These phenyl-phenyl distances are of the order of ~4.9 Å.

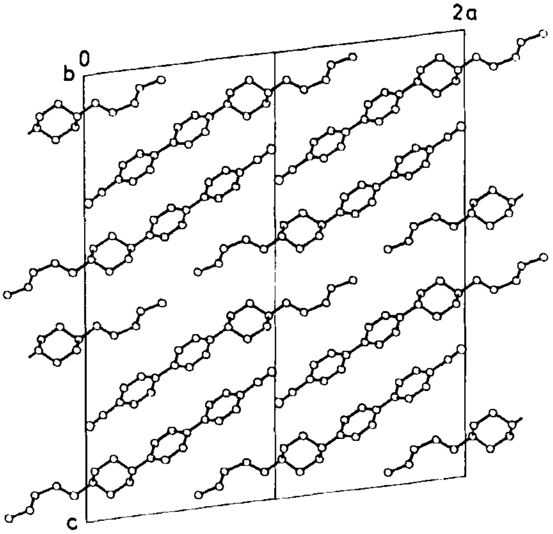

FIGURE 3 Projection of the crystal structure of BCH5CN along the *b*-axis.

Further to the stacking along the *b*-axis and the packing of the molecules, the cyano-groups also form infinite dipole-dipole sequences with a head-to-tail alternation. All these distances are found to be ~3.5 Å. It should here be pointed out that such an infinite cyano-group stacking has also been verified for some kinds of molecules in the crystalline state, *e.g.* substituted cyano-cyclohexylcyclohexanes.[7]

The length of the *b*-axis at ~5.6 Å is rather similar to the packing distance of two cyclohexyl groups, and in this respect, no molecular overlapping is involved in the elementary cell along the *b*-axis.

It is clearly shown in Figure 3 that in the crystalline state, overlapping of the cyano-groups and the biphenyl groups does not occur, but nevertheless, overlapping could easily be achieved through a minor displacement of the molecules along their longest axis at the liquid crystalline phase transition.

The molecular packing of BCH30 is shown in Figure 4. Here one also finds a head-to-tail alternation and the biphenyl groups lying in $y \sim 0.4$ and $y \sim 0.9$. The alternating long axes of the molecules are parallel as demonstrated in Figure 5. The distance between the two antiparallel biphenyls is ~4.9 Å. The phenyl rings are tilted with respect to the phenyl rings of the neighboring biphenyl group. Perpendicular to the *c*-axis, one has layers built up from the nonpolar cyclohexylpropyl unit alternating with the layers of biphenyl groups.

The liquid crystalline state

In the smectic temperature range, the X-ray patterns of unoriented samples of BCH50, BCH52 and BCH54 show sharper inner and outer rings,

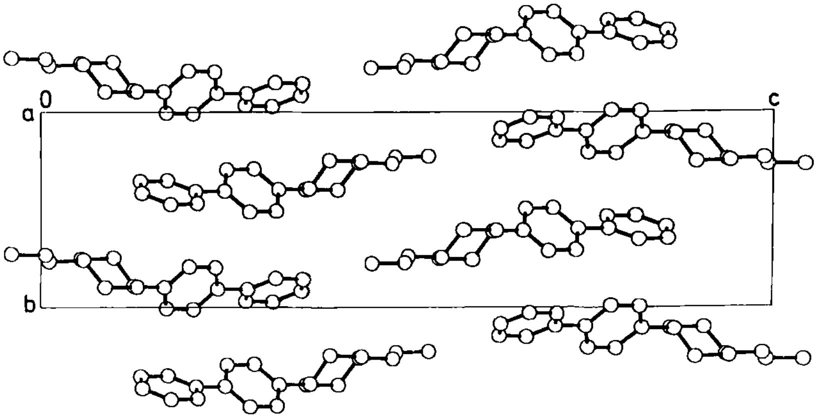

FIGURE 4 Projection of the crystal structure of BCH30 along the *a*-axis. (The figure contains only complete molecules).

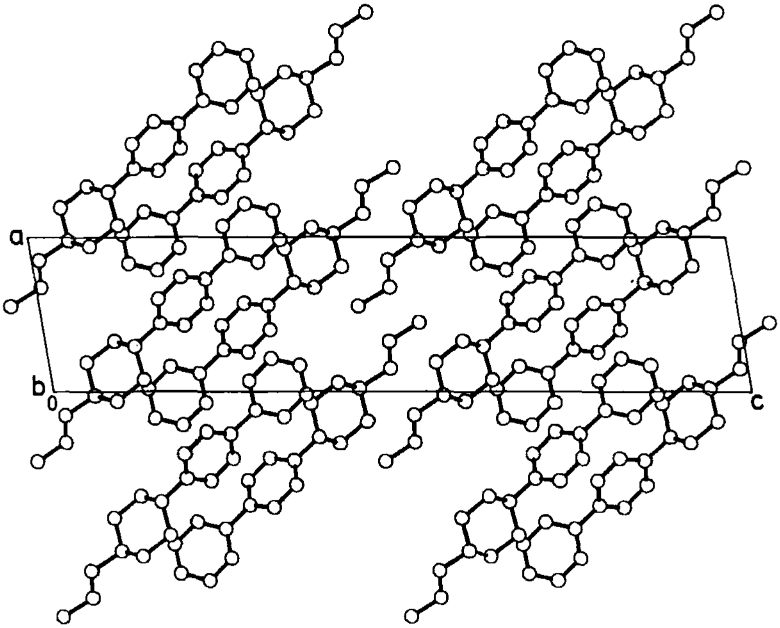

FIGURE 5 Projection of the crystal structure of BCH30 along the *b*-axis. (The figure contains only complete molecules).

whereas the oriented samples show sharp inner reflections and outer spots with additional sharp reflections. All these results are typical for crystalline smectic B-phases.

In Figure 6, the intensity profiles parallel to the c^*-axis are presented. One finds *ABA* stackings for BCH52 and BCH54, whereas BCH50 forms *ABCA* sequences. Similarly, BCH30 shows a B-type X-ray pattern, but as a result of the cooling procedure, a homeotropic orientation is obtained. The X-ray beam is then parallel to the c-axis.

The X-ray patterns of BCH7CN in unoriented as well as in the oriented state confirmed the smectic phase to be an A in type.

In the hexagonal smectic B-cell, the intermolecular distances d can be assumed to be equivalent to the lattice dimensions a and b, whereas the molecular length L is related to the thickness of the layer C as crystallographic axis. The results of the X-ray investigations pertaining to the smectic phases of the compounds investigated are presented in Table VII. Compared with values for compounds having only aromatic six-membered ring with $d \sim 4.9$ Å, the analogous d values of the biphenylcyclohexanes are of the order approximately 5.4 Å as a result of the cyclohexyl group.

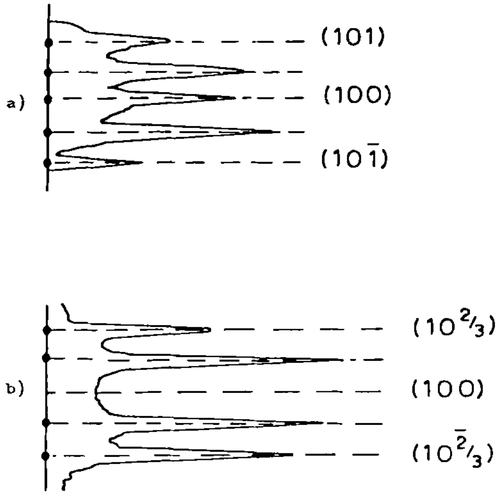

FIGURE 6 Intensity profiles along the outer spots parallel to c^*: a) *ABA* stacking of BCH52, BCH54 and b) *ABCA* stacking of BCH50.

In Figure 7, the temperature dependence of the intermolecular distance d is presented for the compounds studied. This dependence is slightly greater for the A phase of BCH7CN, and somewhat less for the B phases of the compounds described. The thickness C in all the phases is practically independent of the temperature.

The calculated lengths L of the molecules are based on the van der Waals radii. These calculated data are in good agreement with the data for the crystalline states of BCH5CN and BCH30.

The calculated L for the smectic B phases is somewhat larger than the experimental C. The difference $x = L - C$ increases in relation to the

TABLE VII

X-ray data for the smectic phases

	T[K]	C[Å]	L[Å]	x[Å]	d[Å]
BCH30	353	18.8	18.3	−0.5	5.4
BCH50	343	20.4	20.6	0.2	5.5
BCH52	393	22.4	22.9	0.5	5.4
BCH54	423	23.5	25.2	1.7	5.4
BCH7CN	373	35.4	25.2	−10.2	5.3
$BCH5NH_2$	403	19.8	21.6	1.8	5.2

C: thickness, L: calculated molecular length, x: L-C, d: intermolecular distance.

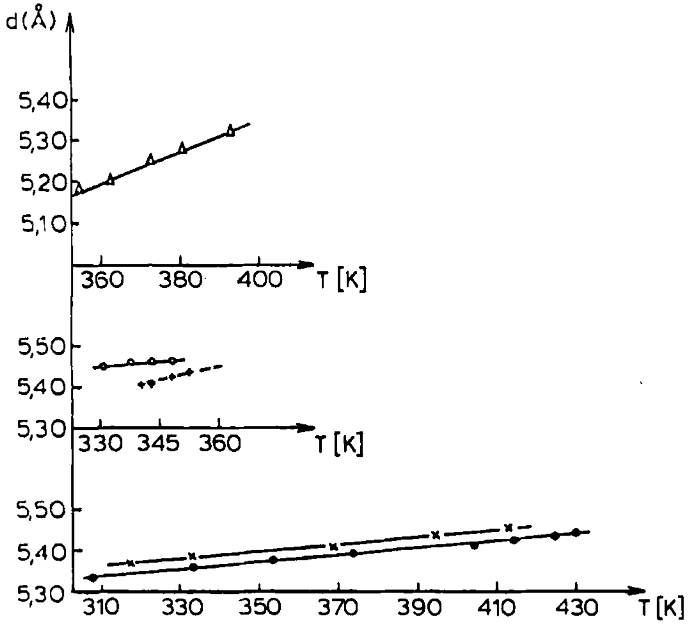

FIGURE 7 Temperature dependence of the intermolecular parameter *d* for the smectic phases: △ BCH7CN; + BCH30; ○ BCH50; × BCH52; ● BCH54

length of the alkyl group. This is due to the fact that the probability of thermal fluctuations as well as for the occurrence of different conformations increases as the alkyl chain becomes longer.

In the smectic A phase of BCH7CN, and likewise in the nematic state, a ratio $C/L \sim 1.4$ results. In the nematic state of BCH5CN, with experimental $d_{\|} = 30.3$ Å and calculated $L = 22.9$ Å, a ratio $d_{\|}/L \sim 1.3$ is obtained. For these cyano-group containing compounds, a partial bilayer model should be discussed. This is presented in Figure 8. The partial bilayer model, following from the experimental *C* value in comparison with the calculated molecular length, is shown assuming a fully extended conformation for the alkyl chain and full ordering. This bilayer model is in agreement with the single crystal data of BCH5CN, as two neighboring molecules are connected nearly in the same manner.

For the cyano-biphenyls, a partial bilayer model is very often discussed.[8,9] Here the cyano-group overlaps with the phenyl ring. If we assume in our case that we have conformational changes occurring in the alkyl group, as well as thermal vibrations, the calculated molecular length becomes smaller. Moreover, de Vries[10] has discussed the importance of

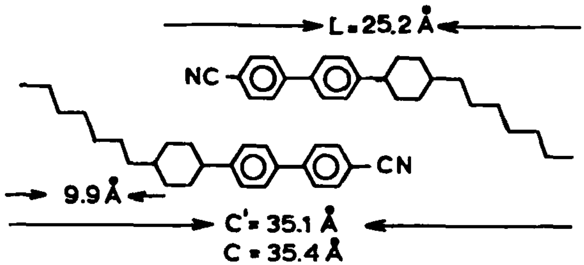

FIGURE 8 Bilayer model for the smectic and nematic states of BCH7CN without thermal fluctuations and assuming a perfect order: *C*: experimental; *L*: calculated; *C'*: *L* plus non-overlapping molecular part.

order in the smectic phases, also resulting in smaller calculated molecular lengths. A realistic order parameter, for example of $S \sim 0.8$, leads to $\zeta \sim 21°$ and a shortening of the molecular length in Figure 8 of 2–3 Å. In this respect, we think that the partial bilayer model of the cyano-biphenyls is realistic also for our cyano-biphenylcyclohexanes.

Acknowledgments

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References

1. R. Eidenschink, W. Erdmann, J. Krause and L. Pohl, 10. Freiburger Arbeitstagung Flüssigkristalle, Freiburg, March 1980.
2. R. Eidenschink, *Kontakte (Merck)* **1**, 15 (1979).
3. H. T. Müller, Ph.D. thesis, Darmstadt, 1982.
4. H. T. Müller and W. Haase, to be published.
5. W. Haase and H. Paulus, *Mol. Cryst. Liq. Cryst.*, in press; and literature cited therein.
6. A. J. Leadbetter, M. A. Mazid and K. M. A. Malik, *Mol. Cryst. Liq. Cryst.*, **61**, 39 (1980).
7. W. Haase and H. Paulus, presented at the Seventh International Liquid Crystal Conference, Bordeaux, 1978, and to be published.
8. A. J. Leadbetter, R. M. Richardson and C. N. Colling, *J. Phys.* (Paris), **36**, 37 (1975).
9. F. Hardouin, A. M. Levelut, G. Sigaud, Nguyen Hun Tinh and M. F. Achard, presented at the Ninth International Liquid Crystal Conference, Bangalore, 1982.
10. A. de Vries, presented at the Ninth International Liquid Crystal Conference, Bangalore, 1982.