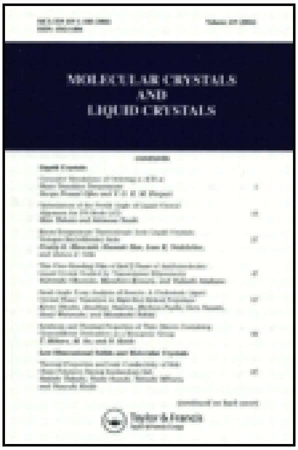

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# Comparison of the Crystal and Molecular Structures of Three Similar 4-Heptyl-biphenyl Compounds: 4-Heptyl-4′-cyanobiphenyl, 4-Heptyl-3′-cyanobiphenyl, and 4-Heptyl-4′-nitrobiphenyl

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# Comparison of the Crystal and Molecular Structures of Three Similar 4-Heptyl-biphenyl Compounds: 4-Heptyl-4′-cyanobiphenyl, 4-Heptyl-3′-cyanobiphenyl, and 4-Heptyl-4′-nitrobiphenyl

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*The structure of 4-heptyl-4′-cyanobiphenyl (7CB4), 4-heptyl-3′-cyanobiphenyl (7CB3), and 4-heptyl-4′-nitrobiphenyl (7NB4) have been investigated at 22°C in the crystalline phase to gain insight into the influence of packing arrangements by intermolecular interactions and of conformation of similar compounds by varying the terminal part of the molecule. The compound 7CB4 exhibits a nematic liquid-crystalline phase that is not present for the other two compounds. The packing of the three compounds is quite different, although two of them belong to the same space group, $P2_1/a$.*

**Keywords:** conformation; packing arrangement; structures of 4-heptyl-biphenyls

## INTRODUCTION

The crystal and molecular structures of the homologues 4-$n$-alkyl-4′-cyanobiphenyls ($n$CB4) with $n = 1$–11 have been investigated in previous studies [1–9], and general as well as comparative conclusions have been drawn concerning conformations and packing arrangements [4,9]. Strong dipolar interactions between the CN groups are one of the features influencing the arrangements of the molecules that crystallize in the centrosymmetric space group $P2_1/c$ (or equivalent

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$P2_1/a$ or $P2_1/n$) with the exception of 2CB4, which shows a second polymorph belonging to the polar space group $P2_1$ [1].

Another homologous series of cyanobiphenyls has been investigated with an alkoxy chain and a hydroxyl terminal group attached to the alkoxy chain [10]. A change of packing arrangement has been detected with an alkoxy chain length $n$ above six methylene groups. The homologues with $n = 7$–$11$ crystallize in space group P2/a and are packed in head–head, tail–tail fashion with strong dipolar interaction of the cyano groups and the hydroxyls involved in hydrogen bonding. For the lower homologues, three to five hydrogen bonds exist between the hydroxyls and the cyano group. The turning point in packing arrangements is represented by $n = 6$ [4-(6-hydroxyhexyloxy)-4′-cyanobiphenyl, H6CBP], which crystallizes in P-1, and two molecules of different conformation form the asymmetric unit [11]. The packing resembles that of the larger homologues.

The turning point for nCB4 occurs also with $n = 6$ in chain arrangements. However, the crystal structures of $n$CB4 compounds with $n \geq 7$ show a distinct odd–even effect with closely arranged CN groups lined up in an infinite chain for even, but for odd $n$, CN and the phenyl groups are close to each other [9]. For lower homologues, a similar grouping is not present [9]. Compounds with $n = 6$ belong to neither of these packing modes.

Differences of the two homologous series exist in their liquid-crystalline behavior. The cyanobiphenyl structures with terminal hydroxyl groups of H$n$CBP exhibit nematic phases only, whereas the cyanobiphenyls with terminal alkyl groups ($n$CB4) lead to a variety of liquid-crystalline phases: crystalline–nematic–isotropic for $n = 5, 6, 7$, which also holds for 4-cyano-4′-alkoxybiphenyl ($n$OCB4) replacing the alkyl group of $n$CB4 by an alkoxy one (cf. [12]). However, for $n = 8, 9$, the phase sequence for these two series consists of crystalline–smectic A–nematic–isotropic, and for $n = 10, 12$, the nematic phase is missing in the sequence despite strong dipolar cyano interactions for all the compounds with longer wing groups.

Therefore, it is interesting to introduce other structural features and to evaluate differences in crystal structures and thermotropic phase behavior of similar compounds [i.e., those with $n = 7$; e.g., 7CB4 to 4-heptyl-4′-nitrobiphenyl (7NB4) or 4-heptyl-3′-cyanobiphenyl (7CB3)], which exhibit small variations in the terminal groups.

The liquid-crystalline nematic phase for 7CB4 exists near room temperature with the phase sequence (temperature in °C) cr 28.5, n 42.5 i.

The changes from the low temperature form at $-33$°C [9] to the ambient-temperature structure are of interest because they provide hints for the structure in the liquid-crystalline phase. In contrast, the compound 7CB3 shows a crystalline phase only with a low melting point (mp) of 33.2°C, as does 7NB4 with a mp of 46.5°C.

It was our goal to investigate the crystal structures of 7CB4, 7CB3, and 7NB4 at the same temperature (22°C), which is close to the crystalline–nematic phase transition of 7CB4 and to the melting point of 7CB3. Additional structural information will be thus available about changes in the vicinity of the transition points.

## EXPERIMENTAL: STRUCTURE DETERMINATION AND REFINEMENT

The compounds have been synthesized in the laboratory of R. Dabrowski, Military Academy of Technology, Warsaw, Poland, and their intermolecular interactions in benzene solutions was studied by nonlinear dielectric effects [13,14]. The data collection of single crystals has been performed on a CAD4 single-crystal diffractometer with monochromatized $MoK_{\alpha}$ radiation, and the MoLEN package (Enraf Nonius, Delft) [15] has been used for data processing and refinement against F. The starting model has been obtained by SIR97 [16]. The hydrogen atoms were placed at their respective sites and not refined with respect to their position nor their isotropic B values. The crystallographic data are summarized in Table 1, and the fractional atomic coordinates of two of the structures (7CB3, 7NB4) are collected in Tables 2 and 3. They have been deposited at the Cambridge Crystallographic Data Centre along with the bond lengths and bond angles (7CB3: CCDC 286249; 7NB4: CCDC 286251). The fractional atomic coordinates of 7CB4 are similar to the ones published [9] and therefore are not listed here; they have been deposited at the Cambridge Crystallographic Data Centre only (CCDC 286250). Figures 1–4, representing the conformation and packing arrangements, have been produced with Schakal92 [17].

## RESULTS AND DISCUSSION

### Molecular Geometry and Conformation

Figure 1 represents the molecular structures and atom labeling of the three structures investigated. 7CB4 consists of two molecules in the asymmetric unit of different conformation as can be deduced by the torsion angles concerning the three least squares planes (Table 4): benzene ring 1, benzene ring 2, and the plane through the backbone of the all trans alkyl chains. It should be noted that the shape of the

**TABLE 1** Summary of Crystallographic Data of 7CB4, 7CB3, and 7NB4 Collected at 22°C

| Parameter | 7CB4 | 7CB3 | 7NB4 |
|---|---|---|---|
| Molecular formula | $C_{20}H_{23}N_1$ | $C_{20}H_{23}N_1$ | $C_{19}H_{23}N_1O_2$ |
| Formula weight (g/mol) | 277.41 | 277.41 | 297.40 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | P-1 | $P2_1/a$ | $P2_1/a$ |
| a (Å) | 9.747 (3) | 10.120 (3) | 10.452 (6) |
| b (Å) | 11.524 (3) | 11.339 (1) | 10.485 (1) |
| c (Å) | 15.861 (4) | 14.700 (8) | 15.304 (12) |
| $\alpha$ (°) | 91.66 (2) | 90 | 90 |
| $\beta$ (°) | 99.00 (2) | 104.90 (3) | 94.86 (3) |
| $\gamma$ (°) | 107.27 (2) | 90 | 90 |
| V(Å)$^3$ | 1674.9 (9) | 1630 (1) | 1671 (2) |
| Z | 4 | 4 | 4 |
| $D_{cal}$ (g/cm$^3$) | 1.10 | 1.13 | 1.18 |
| $\mu$ (MoK$\alpha$) (cm$^{-1}$) | 0.6 | 0.6 | 0.7 |
| $\lambda$ (MoK$\alpha$) (Å) | 0.71073 | 0.71073 | 0.71073 |
| Number of reflections (lattice parameter refinement) | 25 | 25 | 25 |
| Scan range in $\Theta$ (°) | 10–20 | 5–13 | 7–20 |
| Reflections collected | 6306 | 2400 | 4344 |
| Unique data | 5925 | 2248 | 2036 |
| Data collection [$<\Theta<$] | 1–25 | 1–23 | 1–22 |
| $I_0 > 3\sigma$ | 3098 | 1252 | 1129 |
| Parameters refined | 379 | 190 | 199 |
| F (000) | 600 | 600 | 640 |
| R | 0.053 | 0.079 | 0.044 |
| $R_w$ | 0.072 | 0.091 | 0.053 |
| Highest peak (e/Å$^3$) | 0.19 (3) | 0.26 (7) | 0.16 (3) |
| Crystal color | Colorless | Colorless | Colorless |
| Crystal size (mm$^3$) | 0.7 × 0.7 × 0.55 | 0.7 × 0.7 × 0.5 | 1.1 × 0.7 × 0.07 |

two molecules of the structures determined at −33°C [9] and at 22°C near the phase transition are almost identical with negligible changes in positional accuracy, but the displacement parameters increase considerably. Negative twists of torsion angles in Table 4 transform to positive ones by considering the centrosymmetric related molecules and vice versa. The conformational changes from molecule 1 to molecule 2 of 7CB4 are predominantly caused by packing effects because both molecules are identical in constitution. The twist $\varphi$ between the two benzene rings lies in the established range. The aliphatic chain is twisted by an angle $\delta$ out of the benzene plane 2 by about 20.6° for molecule 1 and 6.8° for 2 (corresponding torsion angles

**TABLE 2** Fractional Coordinates and Isotropic Displacement Parameters $B_{eq}$ of 4-Heptyl-3′-cyanobiphenyl (7CB3) at 22°C (Estimated Standard Deviations in Parenthesis)

| Atom | x | y | z | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| N1 | –0.2350(4) | 0.7669(4) | 0.4813(3) | 8.0(1) |
| C01 | –0.1903(5) | 0.6970(4) | 0.4428(3) | 5.6(1) |
| C1 | –0.1489(4) | 0.4903(4) | 0.4148(3) | 4.7(1) |
| C2 | –0.1331(4) | 0.6083(4) | 0.3931(3) | 4.2(1) |
| C3 | –0.0656(4) | 0.6423(4) | 0.3260(3) | 4.4(1) |
| C4 | –0.0081(4) | 0.5586(4) | 0.2780(3) | 3.8(1) |
| C5 | –0.0237(4) | 0.4400(4) | 0.3007(3) | 4.9(1) |
| C6 | –0.0915(5) | 0.4075(4) | 0.3664(3) | 5.2(1) |
| C7 | 0.0633(4) | 0.5931(4) | 0.2068(3) | 3.9(1) |
| C8 | 0.1126(4) | 0.7064(4) | 0.2017(3) | 5.1(1) |
| C9 | 0.1794(5) | 0.7375(4) | 0.1342(3) | 5.2(1) |
| C10 | 0.2059(4) | 0.6590(4) | 0.0699(3) | 4.4(1) |
| C11 | 0.1561(5) | 0.5457(5) | 0.0752(3) | 5.7(1) |
| C12 | 0.0887(5) | 0.5140(4) | 0.1424(3) | 5.4(1) |
| C13 | 0.2792(4) | 0.6983(4) | –0.0029(3) | 5.2(1) |
| C14 | 0.3159(4) | 0.6030(5) | –0.0629(3) | 5.0(1) |
| C15 | 0.3906(4) | 0.6494(5) | –0.1331(3) | 5.1(1) |
| C16 | 0.4355(4) | 0.5532(4) | –0.1905(3) | 4.7(1) |
| C17 | 0.5048(4) | 0.6005(4) | –0.2628(3) | 4.7(1) |
| C18 | 0.5542(5) | 0.5031(4) | –0.3184(3) | 5.3(1) |
| C19 | 0.6291(5) | 0.5513(5) | –0.3883(3) | 6.7(1) |

are −22.9° and 176.3°) and deviate considerably from the respective torsion angle of −90.3° for 5CB4, which is representative of a gauche conformation between the benzene ring 2 and the methylene backbone in an all trans conformation. The C−C bond length of the alkyl chain is about 0.02 Å smaller then the empirically established CCDC value of 1.531 Å and also found for similar alkyl groups in materials is close to a thermal phase transition. The twisting of the two benzene rings is almost the same for 7NB4 and 7CB3 with 16.6° and 17.6°, respectively, but large differences occur for the twisting angle between the least-squares plane of the alkyl chain and the benzene ring 2 with 29.4° for 7NB4 and 9.8° for 7CB3 (Table 4), which are caused by packing arrangements as deduced from the results for 7CB4. The measured C−C bonds in the alkyl groups are about 0.01 Å longer than for 7CB4.

## Packing Arrangements

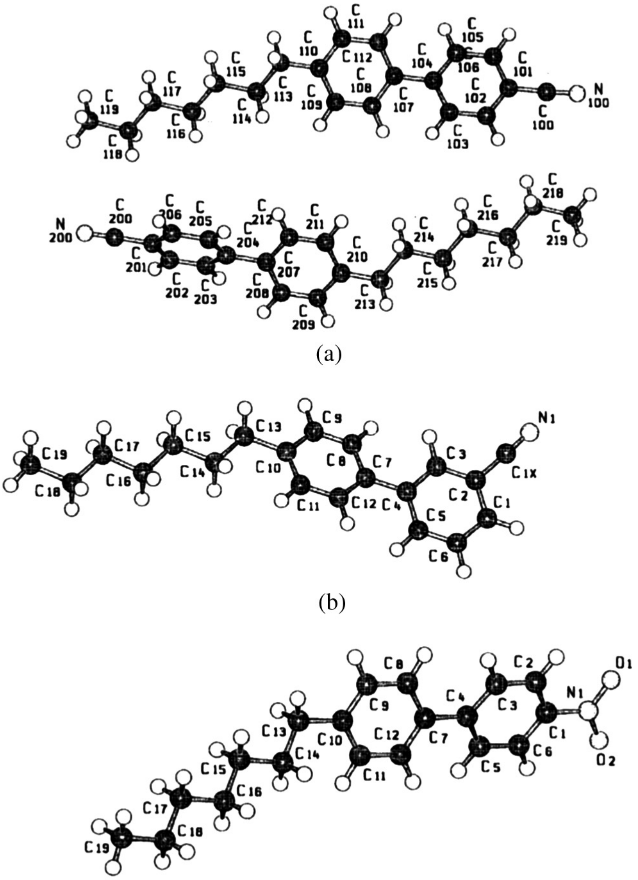
All three structures investigated possess four molecules in the unit cell with 7CB4 belonging to space group P-1 and 7CN3 and 7NB4 to P$2_1$/a. Nevertheless, the packing arrangements of the three compounds are

**TABLE 3** Fractional Coordinates and Isotropic Displacement Parameters $B_{eq}$ of 4-Heptyl-4′-nitrobiphenyl (7NB4) at 22°C (Estimated Standard Deviations in Parenthesis)

| Atom | x | y | z | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| O1 | –0.4665(2) | 0.0367(2) | –0.1265(2) | 8.75(7) |
| O2 | –0.3779(2) | 0.1961(2) | –0.1842(1) | 7.70(6) |
| N1 | –0.3804(2) | 0.1148(2) | –0.1279(2) | 5.71(6) |
| C1 | –0.2761(3) | 0.1112(3) | –0.0574(2) | 4.57(6) |
| C2 | –0.2833(3) | 0.0293(3) | 0.0101(2) | 6.63(8) |
| C3 | –0.1869(3) | 0.0277(3) | 0.0771(2) | 6.58(8) |
| C4 | –0.0815(2) | 0.1068(3) | 0.0774(2) | 4.33(6) |
| C5 | –0.0782(3) | 0.1879(3) | 0.0072(2) | 5.91(8) |
| C6 | –0.1739(3) | 0.1920(3) | –0.0606(2) | 5.91(8) |
| C7 | 0.0233(2) | 0.1038(3) | 0.1485(2) | 4.41(7) |
| C8 | 0.0398(3) | 0.0044(3) | 0.2064(2) | 5.61(7) |
| C9 | 0.1415(3) | –0.0002(3) | 0.2702(2) | 5.84(8) |
| C10 | 0.2314(3) | 0.0940(3) | 0.2795(2) | 5.02(7) |
| C11 | 0.2134(3) | 0.1952(3) | 0.2239(2) | 8.38(9) |
| C12 | 0.1117(3) | 0.2011(3) | 0.1599(2) | 7.91(9) |
| C13 | 0.3445(3) | 0.0834(3) | 0.3473(2) | 6.29(8) |
| C14 | 0.3974(3) | 0.2064(3) | 0.3848(2) | 5.58(7) |
| C15 | 0.5024(3) | 0.1890(3) | 0.4588(2) | 5.64(8) |
| C16 | 0.5503(3) | 0.3129(3) | 0.5006(2) | 5.52(8) |
| C17 | 0.6539(3) | 0.2966(3) | 0.5758(2) | 5.48(8) |
| C18 | 0.7059(3) | 0.4200(3) | 0.6136(2) | 6.25(8) |
| C19 | 0.8105(3) | 0.4039(3) | 0.6873(2) | 7.20(9) |

quite different. Figure 2 represents the molecular arrangement for 7CB4 in two projections. The molecules are placed in head-to-tail fashion by a transformation of the asymmetric unit (two molecules) by $(-x+1, -y+2, -z+2)$ as depicted in Fig. 2a. The two pairs of head-to-tail placed molecules can be regarded as basic units of the unit cell. Pure translation of two head-to-tail arranged molecules considered as a basic unit leads to a continuous molecular string. A single molecular axis can be defined following the continuous string of succeeding molecules and is shown in the projection down the string axis in Fig. 2b. The strings of molecules are placed in parallel and antiparallel fashion. No strong dipolar interaction between the CN dipoles can be formed by this kind of packing in contrast to *n*CB4 with $n = 2$–5 [1].

The arrangement of the 7CB3 molecules are depicted in Fig. 3 in two projections. A head-to-tail arrangement of succeeding molecules is also realized for this compound with a pure shift $(x+1, y, z)$ of the asymmetric unit to obtain the adjacent molecule in Fig. 3a. The axes of the biphenyl and the attached alkyl chain are slightly bent



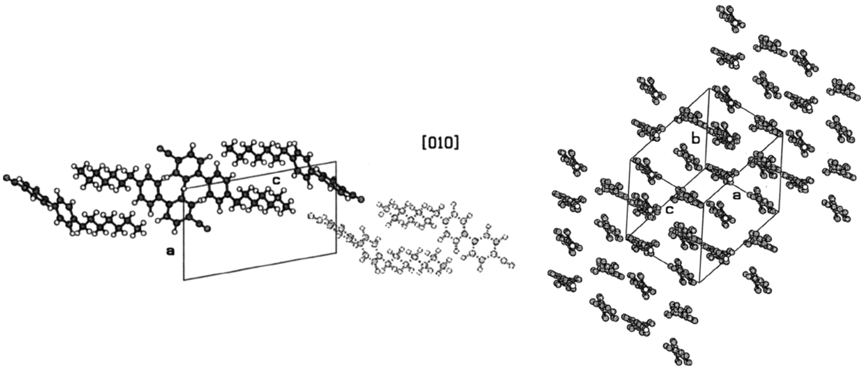
(a)

(b)

(c)

**FIGURE 1** Representation of the conformation and atom labeling of (a) 7CB4 with two molecules in the asymmetric unit, (b) 7CB3 with one molecule, and (c) 7NB4 with one molecule.

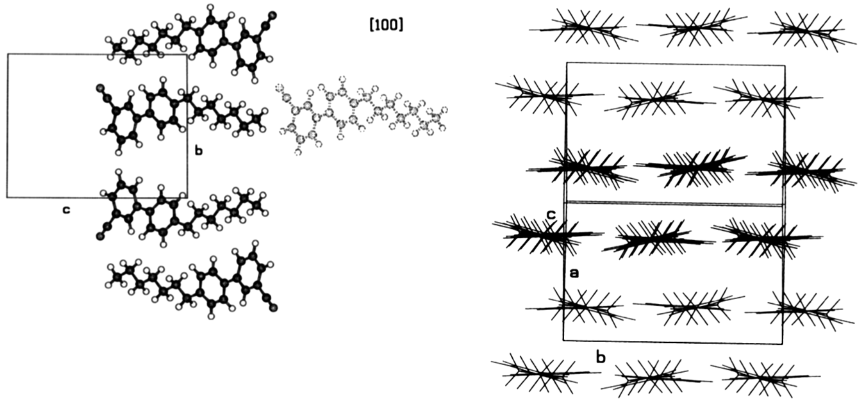
toward each other in one molecule, and the bend is repeated in the same directions of the succeeding molecules, forming the string. Nevertheless, an axis for the continuous string can be easily defined as shown in Fig. 3b. Caused by the symmetry elements of the space group, the bend within a molecule of adjacent strings may show in the opposite direction and the axes of the strings may run parallel or antiparallel. Strong dipolar interactions are not present. It is noteworthy that the packing density of 7CB3 is higher than that for the more linear structure of 7CB4 (cf. Table 1).



(a) (b)

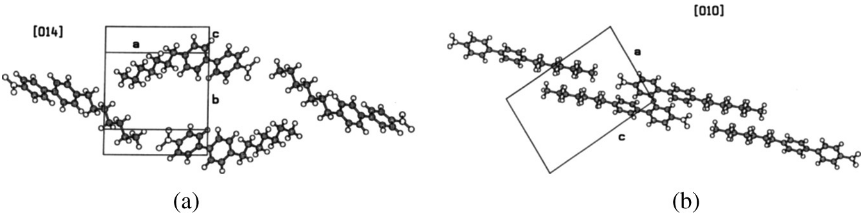
**FIGURE 2** Representation of the packing of 7CB4 in two projections: (a) Projection along b; four molecules are needed to describe the content of the unit cell. The lightly drawn molecules represent succeeding molecules of the original ones in head-to-tail fashion to form strings in continuation. (b) Projection along the string axes. The H atoms are omitted.

The head-to-tail arrangements continues for 7NC4 with no close contacts between the nitro groups (distances N··N > 5, 3 Å, O··O > 4.0 Å) in the structure (Fig. 4a). However, the packing arrangement of



(a) (b)

**FIGURE 3** Representation of the packing arrangement of 7CB3: (a) Projection on the b, c plane; four molecules are needed to describe the content of the unit cell of space group P $2_1/a$. The lightly drawn molecule represents a succeeding molecule in head-to-tail fashion to form strings in continuation. (b) Projection along the string axes.



(a) (b)

**FIGURE 4** Representation of the packing arrangement of 7NB4: (a) Projection of the four molecules of the unit cell, space group $P2_1/a$, rearranged in units of two head-to-tail molecules forming zigzag strings in continuation. [Symmetry operations: $(x, y, z; -3/2+x, 1/2-y, -1+z; -x, 1-y, -z; 3/2-x, 1/2+y, 1-z)$]. (b) Projection along the b axis that shows the molecules as straight entities.

the molecules is different from the one of 7CB3 and has to be discussed in some detail. As outlined in Table 4, the torsion angles between benzene plane 2 and alkyl plane differ considerably for 7NB4 and 7CB3, and this difference is even greater when benzene plane 1 and the alkyl plane is considered. This means that the shape of the molecules is strongly bent in 7NB4. The symmetry relation applied to the asymmetric molecule to produce the succeeding molecule of the string is no longer a pure translation as detected for 7CB3 but rather represents a symmetry element of space group $P2_1/a$ $(-3/2+x, 1/2-y, -1+z)$. The two differently placed molecules form a basic head-to-tail unit, and a pure shift of these two molecules leads to a continuous zigzag string. Next, the opposite running molecule is produced by the inversion symmetry element of the space group $(-x, 1-y, -z)$ in Fig. 4a. To obtain the basic second molecule for the opposite running zigzag string, the fourth symmetry element of space group $P2_1/a$ has to be applied on the asymmetric molecule $(3/2-x, 1/2+y,$

**TABLE 4** Selected Torsion Angles and Angles between Least Squares Planes Through the Appropriate Non-H Positions in Degrees of Two Molecules of 7CB4 and the Ones of 7NB4 and 7CB3

| Torsion angles, Angles between planes | 7CB4 (1) | 7CB4 (2) | 7NB4 | 7CB3 |
|---|---|---|---|---|
| $\tau$ (C3-C4-C7-C8) | 30.0 (3) | –35.1 (3) | 16.4 (4) | 19.1 (6) |
| $\tau$ (C9-C10-C13-C14) | –22.9 (4) | 176.3 (2) | –149.9 (3) | 173.8 (4) |
| $\varphi$ (benzene plane 1–2) | 29.7 (1) | 36.0 (1) | 16.6 (3) | 17.6 (3) |
| $\delta$ (plane 2, alkyl plane) | 20.6 (2) | 6.8 (5) | 29.4 (2) | 9.8 (6) |

$1 - z$). In Fig. 4a, the four space group symmetry of $P2_1/a$ related molecules are depicted but shifted by unit vectors for a better representation. A so-called herringbone packing is obtained, with opposite running molecules stacked up in two different directions.

It should be remarked that a unique string axis containing the axes of the molecules cannot be defined for 7NB4: (i) the conformation of a single molecule exhibits two partial axes, one for the biphenyl moiety and a second one, bent to the first one, along the alkyl chain; and (ii) the zigzag shape of the string again requires the introduction of two partial axes. Nevertheless, it is interesting that the axes of all biphenyls within the structure are parallel, which is not the case for 7CB3. The bend within the molecules and the one of the strings disappears when the molecules are projected along a certain direction on a plane (Fig. 4b).

## CONCLUSIONS

It was shown by a comparative structural investigation that the conformation and packing arrangements as well as the phase sequence of a biphenyl moiety with attached terminal alkyl chain of seven carbon atoms is strongly influenced by the presence and position of a cyano or nitro group at the terminal benzene ring.

The intermolecular van der Waals interaction dominates the packing arrangements, and the polar interactions of the cyano ($N \cdot\cdot N$ distances $> 5$ Å) or nitro terminal groups play a minor role for longer terminal alkyl groups in contrast to the short ones (e.g., for $n$CB4 with $n = 2$–$5$). This finding also contrasts the intermolecular interactions for 7CB4 in benzene solutions as discussed in Ref. [13]. The strong molecular dipoles are compensated in the solid state within a unit cell by their antiparallel counterparts provided by an inversion center of the space group. The basic structure of 7CB4 in a unit cell consists of two molecules with different conformations in contrast to 7CB3 and 7NB4, for which a single conformation was found.

The results of the present structure determination support the idea, also verified by other studies, that the twist of the planes of the benzene rings $\varphi$ in the biphenyl moiety is predominantly influenced by the packing arrangement of the molecules. The same is true for the twisting angle $\delta$ between the all trans terminal alkyl chain and the adjacent benzene ring 2. This means that these two torsional parts of the potential energy exhibit a shallow potential energy function and may be easily influenced by the lowering of the energy by better packing.

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