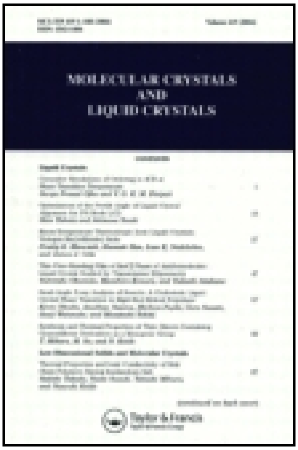

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The Molecular and Crystal Structures of Three 4-(ω-Cyanoalkyloxy)Benzoic Acids and of A 1:1 Ordered Mixed Crystal Of 4-(ω-Cyanobutyloxy)Benzoic Acid and 4-(ω-Cyanopentyloxy)Benzoic Acid Formed by Hydrogen Bonding

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THE MOLECULAR AND CRYSTAL STRUCTURES OF THREE 4-(ω-CYANOALKYLOXY)BENZOIC ACIDS AND OF A 1:1 ORDERED MIXED CRYSTAL OF 4-(ω-CYANOBUTYLOXY)BENZOIC ACID AND 4-(ω-CYANOPENTYLOXY)BENZOIC ACID FORMED BY HYDROGEN BONDING

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The crystal and molecular structures of 4-(ω-cyanobutyloxy)benzoic acid (CN4BS), 4-(ω-cyanopentyloxy)benzoic acid (CN5BS), 4-(ω-cyanohexyloxy)-benzoic acid (CN6BS), as well as 1:1 ordered mixed crystal of 4-(ω-cyanobutyloxy)benzoic acid and 4-(ω-cyanopentyloxy)benzoic acid formed by hydrogen bonding (CN4-5BS) have been determined by single crystal X-ray diffractometry at room temperature and solved by direct methods. The crystals of the three compounds CN4BS, CN5BS, and CN6BS belong to the same monoclinic centrosymmetric space groups No. 14 (the used settings are $P2_1/n$, $P2_1/c$, and $P2_1/n$, respectively), with 4 molecules in the unit cell. The center of symmetry lies between the two carboxylic acid groups of adjacent molecules which are connected by hydrogen bonds. This center of symmetry is missing for the mixed 1:1 compound CN4-5BS, and its crystals belong to the noncentrosymmetric space group Pc with four molecules in the unit cell. The unit cell parameters are, for CN4BS: $a = 4.987(2)$, $b = 8.309(1)$, $c = 27.549(15)$ Å, $\beta = 94.65(3)°$; for CN5BS: $a = 10.799(3)$, $b = 4.9733(6)$, $c = 23.038(7)$ Å, $\beta = 92.60(2)°$; for CN6BS: $a = 15.217(4)$, $b = 4.8994(8)$, $c = 17.839(5)$ Å, $\beta = 92.52(1)°$; for CN4-5BS: $a = 4.963(1)$, $b = 25.962(4)$, $c = 9.234(2)$ Å, $\beta = 99.586(6)°$. The structures were refined by full-matrix least-squares calculations against F to $R = 0.044$ for 2521 unique data ($1839 > 3\sigma$) for CN4BS; to $R = 0.063$ for 2513 unique data ($1602 > 3\sigma$) for CN5BS, which exhibits a disordered conformation; to $R = 0.038$ for 1414 unique data ($883 > 3\sigma$) for CN6BS; and to $R = 0.040$ for 2190 unique data ($1339 > 1\sigma$) for CN4-5BS. The conformation of the ω-cyanoalkoxy chain differs between the two compounds CN4BS and CN5BS, as compared to the mixed compound CN4-5BS, actually consists of these two molecules and leads to different packing arrangements.

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Keywords: crystal structure of 4-(ω-cyanoalkyloxy)benzoic acid; molecular packing; liquid crystals

INTRODUCTION

The relationship between symmetry in hydrogen-bonded benzoic acids and the formation of acentric crystals has been reviewed by examination of 139 compounds extracted from the Cambridge Crystallographic Data File [1] with the result that dimers occur and centric patterns are present. It was proposed that benzoic acid molecules aggregate already in solution and that these aggregates initiate crystal nucleation, and that the local symmetry at the carboxylic acid groups of the solution aggregate biases the final symmetry of the nucleation site. Therefore, dimers may better represent the basic entity of the nucleation process.

A study was undertaken to show the validity of the hydrogen bonding system also in the liquid crystalline state for a homologous series of 4-(ω-cyanoalkyloxy)benzoic acids which provide the necessary mesogenic core by the centric hydrogen bonding pattern [2]. Here we are interested in the influence of the conformation of the ω-cyanoalkoxy chain as wing group on the packing arrangements of the molecules in a crystal, and especially if the idea of the nucleation process of the dimeric molecule holds by avoiding the center of symmetry by cocrystallizing two 4-(ω-cyanoalkyloxy)benzoic acids with different chain lengths of the wing groups as 4-(ω-cyanobutyloxy)benzoic acid with 4-(ω-cyanopentyloxy)benzoic acid from solution.

EXPERIMENTAL—STRUCTURE DETERMINATION AND REFINEMENT

The synthesis of 4-(ω-cyanobutyloxy)benzoic acid (CN4BS), 4-(ω-cyanopentyloxy)benzoic acid (CN5BS) and 4-(ω-cyanohexyloxy)benzoic acid (CN6BS) has been described by Bock [2]. Single crystals suitable for X-ray investigations were obtained by slow crystallization from butylacetate at room temperature. The dissolution of a 1:1 mixture of CN4BS and CN5BS led to crystals of 1:1 aggregates of CN4-5BS. The crystals of CN6BS and CN4-5BS were small and allowed the collection of only a limited amount of X-ray data. The data collection was performed on a CAD4 single crystal diffractometer with MoK$_\alpha$ radiation and the MolEN package (Enraf Nonius, Delft) [3] was used for data processing and refinement against F. The starting model was obtained by SIR97 [4]. The hydrogen atoms were placed at respective sites and not refined with respect to their position and their isotropic B values, with the exception of the hydroxyl hydrogen involved in hydrogen bonding, which were determined by difference Fourier synthesis.

TABLE 1 Summary of Crystallographic Data of CNS4, CNS5, CN6BS, and CN4-5BS

	CN4BS	CN5BS	CN6BS	CN4-5BS
Molecular formula	$C_{12}H_{13}NO_3$	$C_{13}H_{15}NO_3$	$C_{14}H_{17}NO_3$	$C_{25}H_{28}N_2O_6$
Formula weight/g·mol^{-1}	219.24	233.27	247.30	452.51
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P21/n (No.14)	P21/c (No.14)	P21/n (No.14)	Pc (No.7)
a/Å	4.987(2)	10.799(3)	15.217(4)	4.963(1)
b/Å	8.309(1)	4.9733(6)	4.8994(8)	25.962(4)
c/Å	27.549(15)	23.038(7)	17.839(5)	9.234(2)
α/°	90	90	90	90
β/°	94.65(3)	92.60(2)	92.52(1)	99.586(6)
γ/°	90	90	90	90
V/Å^3	1137.9(8)	1236.0(6)	1328.6(5)	1173.2(4)
D_{cal}/g·cm^{-3}	1.28	1.25	1.24	1.28
Z	4	4	4	2
$\mu(MoK_\alpha)/cm^{-1}$	0.9	0.8	0.8	0.9
$\lambda(MoK_\alpha)$/Å	0.71073	0.71073	0.71073	0.71073
Number of reflections for lattice parameter refinement	25	24	25	15
Scan range	$12° < \theta < 25°$	$10° < \theta < 25°$	$6° < \theta < 18°$	$6° < \theta < 17°$
F(000)	464	496	528	480
Reflections collected	2824	2647	1479	2192
Unique data	2521	2513	1414	2190
Significant I's ($>3\sigma$)	1839	1602	883	($>1\sigma$) 1339
Data collection	$1° < \theta < 27°$	$1° < \theta < 27°$	$1° < \theta < 21°$	$1° < \theta < 20°$
Parameters refined	145	172	163	296
R	0.044	0.063	0.038	0.040
R_w	0.065	0.076	0.050	0.040
Highest peak/e·Å^{-3} in $\Delta\rho$	0.18(4)	0.23(6)	0.13(4)	0.21(5)
Crystal color	colorless	colorless	colorless	colorless
Crystal size/mm^3	needle	spherelike	$0.07 \times 0.15 \times 0.6$	$0.04 \times 0.3 \times 0.7$

The crystallographic data are summarized in Table 1 and the fractional atomic coordinates of the four structures collected in Tables 2(a)–2(d). Figures 1–5, representing the conformation and packing, were produced with SCHAKAL92 [5].

RESULTS AND DISCUSSION

Molecular Conformation

The molecular conformation of the homologous compounds CN4BS, CN5BS, and CN6BS can best be represented by dimers consisting of two molecules connected by hydrogen bonds (cf. Figures 1(a)–1(c)). A center of symmetry is located in the center of the hydrogen bonding system which

TABLE 2(a) Atomic Coordinates and Equivalent Isotropic Displacement Factors B_{eq} of CN4BS with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}(Å^2)
O1	0.2673(2)	0.3577(1)	0.51184(4)	5.16(3)
O2	0.3401(3)	0.4799(2)	0.44202(5)	5.36(3)
O3	−0.5541(2)	−0.0104(1)	0.36274(4)	4.43(2)
N1	−1.1979(3)	−0.5638(2)	0.26739(6)	5.64(4)
C1	0.2159(3)	0.3776(2)	0.46657(6)	4.00(3)
C2	0.0053(3)	0.2780(2)	0.44055(5)	3.78(3)
C3	−0.1387(3)	0.1676(2)	0.46532(5)	4.02(3)
C4	−0.3302(3)	0.0681(2)	0.44099(5)	4.04(3)
C5	−0.3757(3)	0.0820(2)	0.39063(5)	3.78(3)
C6	−0.2337(4)	0.1933(2)	0.36540(6)	4.60(3)
C7	−0.0438(4)	0.2905(2)	0.38999(6)	4.59(3)
C8	−0.7003(3)	−0.1344(2)	0.38556(6)	4.27(3)
C9	−0.8574(3)	−0.2243(2)	0.34477(6)	4.14(3)
C10	−0.6702(3)	−0.3147(2)	0.31288(6)	4.16(3)
C11	−0.8042(3)	−0.3612(2)	0.26282(6)	4.43(3)
C12	−1.0257(3)	−0.4745(2)	0.26530(6)	4.09(3)
H1O*	0.547	0.544	0.471	7.0

*Atoms were not refined.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as: $(4/3)*[a^2*B(1,1)+b^2*B(2,2)+c^2*B(3,3)+ab(\cos\gamma)*B(1,2)+ac(\cos\beta)*B(1,3)+bc(\cos\alpha)*B(2,3)]$.

causes the two molecules engaged to consist of the image and corresponding mirror image. The 1:1 aggregate CN4-5BS represents an exception, since a center of symmetry cannot exist because two different molecules CN4BS, CN5BS are joined by hydrogen bonding to form 1:1 ordered mixed crystals (Figure 1(d)) in the same manner as the other molecules of the homologous series. The C-O distances of the carboxylic acid group are listed in Table 3 for the various compounds. Also listed in Table 3 are the data for the hydrogen bonds. The two C-O distances have almost the same bond length for CN4BS and CN5BS but differ slightly for CN6BS and CN4-5BS. The hydrogen bond distances, i.e., O..O distance, range from 2.57 to 2.69 Å. The alkoxy chain is connected in a gauche conformation to the benzene ring (τ(O3-C8-C9-C10) = ±65° (±1.5°)) corresponding to the image and mirror image of the molecule; cf. Table 4. It should be remarked that all the signs of the torsion angles of each compound in Table 4 may be inverted due to the existence of the image and mirror image of each molecule caused by the center of inversion. This statement cannot be proven for the mixed compound since a center of inversion is missing. However, it is likely that crystallites exist which are uniformly built by 1:1 aggregates of the mirror image of the listed

TABLE 2(b) Atomic Coordinates and Equivalent Isotropic Displacement Factors B_{eq} of CN5BS with Their Estimated Standard Deviations in Parentheses

Atom	*x*	*y*	*z*	B_{eq}(Å^2)
O1	0.6031(2)	−0.2529(4)	0.49331(7)	4.35(4)
O2	0.4433(2)	−0.3598(4)	0.43314(7)	4.59(4)
O3	0.6909(1)	0.5158(4)	0.27944(6)	3.94(4)
N1$^{\#}$	1.0429(3)	0.3278(9)	0.0754(2)	6.9(1)
N1A§	0.925(1)	0.861(3)	−0.0222(4)	7.1(3)
C1	0.5416(2)	−0.2213(5)	0.44685(9)	3.36(5)
C2	0.5794(2)	−0.0185(5)	0.40417(9)	3.26(5)
C3	0.6801(2)	0.1471(5)	0.41689(9)	3.60(5)
C4	0.7208(2)	0.3312(5)	0.3769(1)	3.57(5)
C5	0.6580(2)	0.3487(5)	0.32309(9)	3.21(5)
C6	0.5555(2)	0.1871(5)	0.3100(1)	3.64(5)
C7	0.5168(2)	0.0047(5)	0.3501(1)	3.55(5)
C8	0.8003(2)	0.6789(6)	0.2883(1)	4.15(6)
C9	0.8152(2)	0.8320(6)	0.2326(1)	4.59(6)
C10	0.8385(2)	0.6572(6)	0.1804(1)	4.59(6)
C11	0.8485(3)	0.8154(7)	0.1247(1)	5.73(7)
C12	0.8589(3)	0.6422(9)	0.0710(1)	6.79(9)
C13$^{\#}$	0.9607(3)	0.4714(9)	0.0728(2)	4.97(8)
C13A§	0.904(1)	0.761(3)	0.0199(5)	6.2(3)
H1O*	0.580	−0.446	0.530	5.0

For explanation see Table 2(a). #Partial occupancy 75%.
§Partial occupancy 25%.
*Atoms were not refined.

molecules. The cyano group for CN5BS exhibits partial occupancy, causing a disordered structure, which leads to interactions of two adjacent dipoles in the crystal discussed later. The terminal cyano group is in gauche conformation for all the compounds except for the CN4BS in the mixed compound CN4-5BS. Some displacement values B_{eq} of the alkoxy chain are rather high (Table 2(d)), the origin of which cannot be evaluated due to the limited data set. The corresponding torsion angles have opposite signs in respect to τ(O3-C8-C9-C10) for even-numbered C atoms in the alkoxy chain but the same sign for odd-numbered C atoms, excluding the partial occupancy for CN5BS, and are clearly visible in Figures 1(a)–1(d).

Molecular Packing

The arrangement of the molecules of the homologous series investigated exhibits interesting features within the crystallites. The compounds forming dimers are packed in the centrosymmetric space group No. 14 listed in the International Tables [6] in the monoclinic space group $P2_1/c$ or $P2_1/n$,

TABLE 2(c) Atomic Coordinates and Equivalent Isotropic Displacement Factors B_{eq} of CN6BS with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	$B_{eq}(Å^2)$
O1	0.4039(2)	−0.3644(5)	0.5410(1)	4.99(6)
O2	0.5455(1)	−0.2493(5)	0.5510(1)	4.66(6)
O3	0.3838(2)	0.5259(5)	0.7938(1)	4.76(6)
N1	0.3377(2)	1.1902(9)	1.2054(2)	8.1(1)
C1	0.4686(2)	−0.2191(7)	0.5696(2)	3.97(8)
C2	0.4458(2)	−0.0172(7)	0.6269(2)	3.87(8)
C3	0.3599(2)	0.0118(7)	0.6505(2)	4.29(9)
C4	0.3414(2)	0.1953(7)	0.7052(2)	4.14(8)
C5	0.4087(2)	0.3556(7)	0.7376(2)	3.93(8)
C6	0.4942(2)	0.3323(7)	0.7149(2)	4.07(8)
C7	0.5118(2)	0.1446(7)	0.6592(2)	4.04(8)
C8	0.4512(2)	0.6907(8)	0.8309(2)	4.88(9)
C9	0.4067(3)	0.8631(8)	0.8885(2)	5.3(1)
C10	0.3704(3)	0.7016(8)	0.9514(2)	5.6(1)
C11	0.3233(3)	0.8796(9)	1.0075(2)	5.9(1)
C12	0.2810(3)	0.720(1)	1.0661(2)	7.3(1)
C13	0.2341(3)	0.890(1)	1.1236(2)	7.2(1)
C14	0.2922(2)	1.0565(9)	1.1700(2)	5.8(1)
H1O*	0.423	−0.536	0.499	6.5

For explanation see Table 2(a).
*Atoms were not refined.

respectively. But the mixed compound CN4–5BS crystallizes in the non-centrosymmetric space group Pc (No. 7). Differences in packing arrangements can already be deduced from the length of the unique axis **b** for the single compounds (cf. Table 1) of the same monoclinic space groups. The unit cell parameter **b** represents the smallest length for CN5BS and CN6BS, but for CN4BS and the mixed compound the smallest parameter is **a**. The size of the smallest unit cell parameter comes close to 5 Å for all compounds. Comparing CN4BS and CN4–5BS, they differ considerably in the size of the unique axis **b**.

The observed three different types of packing are represented in Figures 2–5. CN4BS exhibits a herringbone structure projected in [100] direction, as depicted in Figure 2(a). The adjacent cyano groups in the **b-c** plane point in different directions, forming in [001] projection almost a right angle, as represented in Figure 2(b), and are far apart (N..N distance 6.23 Å). A strong dipolar interaction cannot occur. However, the cyano groups of adjacent parallel running molecules, shifted in **a,** are much closer (cf. Figure 2(b)) but still too far to interact significantly (N..N distance 4.98 Å; the length of **a**).

TABLE 2(d) Atomic Coordinates and Equivalent Isotropic Displacement Factors B_{eq} of CN4-5BS with Their Estimated Standard Deviations in Parentheses

Atom	*x*	*y*	*z*	B_{eq}(Å^2)
O101	1.0364(6)	0.2342(1)	0.0337(3)	5.90(9)
O102	0.9404(7)	0.3124(1)	0.1220(3)	4.70(8)
O103	1.6784(6)	0.3769(1)	−0.3401(3)	4.63(8)
O201	0.6099(6)	0.2652(1)	0.2627(3)	3.70(8)
O202	0.6858(6)	0.1869(1)	0.1839(3)	5.28(8)
O203$^{\#}$	−0.060	0.1234(1)	0.645	4.52(9)
N101	1.372(1)	0.4903(2)	−0.9265(5)	7.1(1)
N201	0.314(2)	0.0131(3)	1.2411(8)	13.3(2)
C101	1.0802(9)	0.2837(2)	0.0337(5)	3.7(1)
C102	1.239(1)	0.3063(2)	−0.0574(5)	5.2(1)
C103	1.3828(9)	0.2767(2)	−0.1411(4)	3.3(1)
C104	1.5303(9)	0.2991(2)	−0.2312(5)	3.4(1)
C105	1.5373(9)	0.3522(2)	−0.2481(5)	3.3(1)
C106	1.3974(9)	0.3830(2)	−0.1619(6)	4.7(1)
C107	1.2514(9)	0.3592(2)	−0.0776(5)	3.7(1)
C108	1.809(1)	0.3460(2)	−0.4348(5)	4.6(1)
C109	1.926(1)	0.3834(3)	−0.5380(6)	7.4(2)
C110	1.713(1)	0.4126(2)	−0.6418(7)	6.4(2)
C111	1.839(2)	0.4508(2)	−0.7414(6)	11.3(2)
C112	1.559(2)	0.4806(3)	−0.8485(6)	10.1(2)
C201	0.5809(8)	0.2200(2)	0.2600(5)	4.1(1)
C202	0.3922(8)	0.1926(2)	0.3580(4)	2.4(1)
C203	0.255(1)	0.2242(2)	0.4413(6)	5.1(1)
C204	0.0950(9)	0.2031(2)	0.5424(5)	4.3(1)
C205	0.0767(9)	0.1515(2)	0.5493(4)	4.7(1)
C206	0.217(1)	0.1188(2)	0.4639(5)	5.0(1)
C207	0.380(1)	0.1388(2)	0.3595(5)	5.3(1)
C208	−0.199(1)	0.1521(2)	0.7437(5)	5.2(1)
C209	−0.311(1)	0.1170(2)	0.8403(5)	4.0(1)
C210	−0.096(1)	0.0889(2)	0.9364(5)	6.9(1)
C211	−0.213(2)	0.0579(3)	1.0318(9)	12.8(3)
C212	−0.150(2)	0.0117(4)	1.0725(9)	12.6(3)
C213	0.104(1)	0.0166(3)	1.1692(6)	7.2(2)
H12O*	0.790	0.290	0.189	8.0
H11O*	0.859	0.206	0.109	8.0

For explanation see Table 2(a).
#Position in x, z fixed.
*Atoms were not refined.

A projection along the smallest unit cell dimension, i.e., along [010] for CN5BS and CN6BS, represents different patterns in contrast to Figure 2(a), and they resemble each other as deduced from Figures 3(a) and 4(a). Long strings are formed lying in a plane and tilted versus the **b**-axis. The molecules are shifted parallel by some amount from one dimer to the next

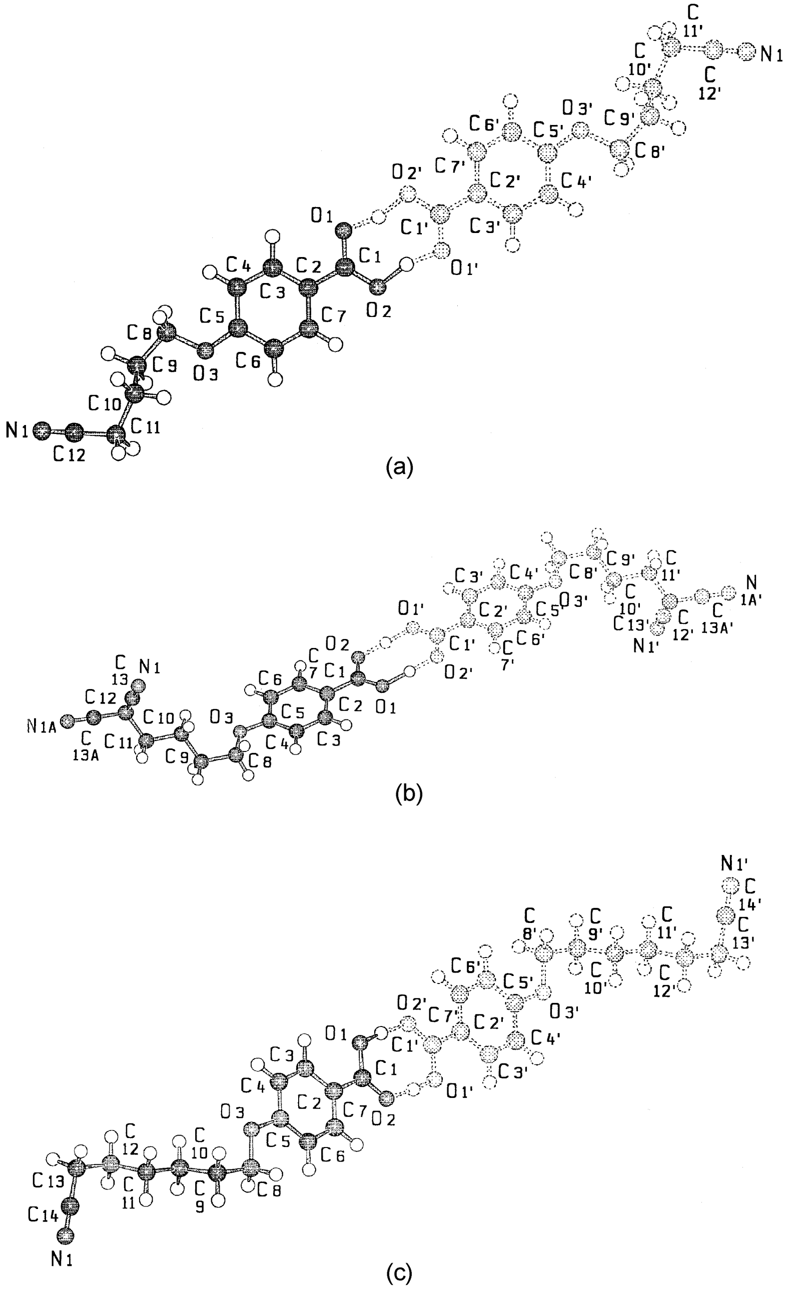


FIGURE 1 Representation of the conformation and atom labeling of (a) CN4BS, (b) CN5BS, (c) CN6BS, and (d) CN4-5BS.

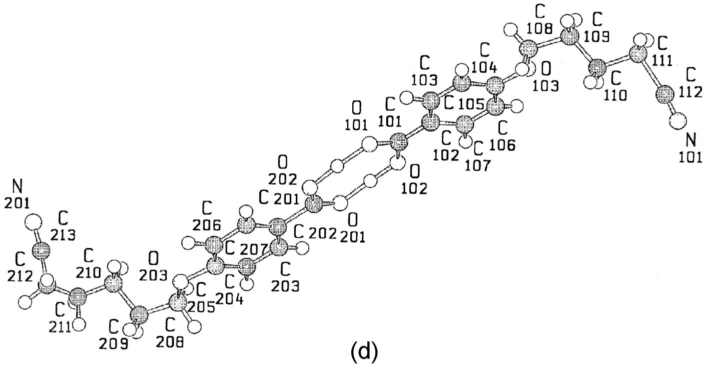


FIGURE 1 (*Continued.*)

due to the one gauche conformation in the alkoxy group. The terminal cyano groups are in close contact in a string for CN5BS, as represented in Figure 3(b), with partial occupancy causing disorder as shown in this

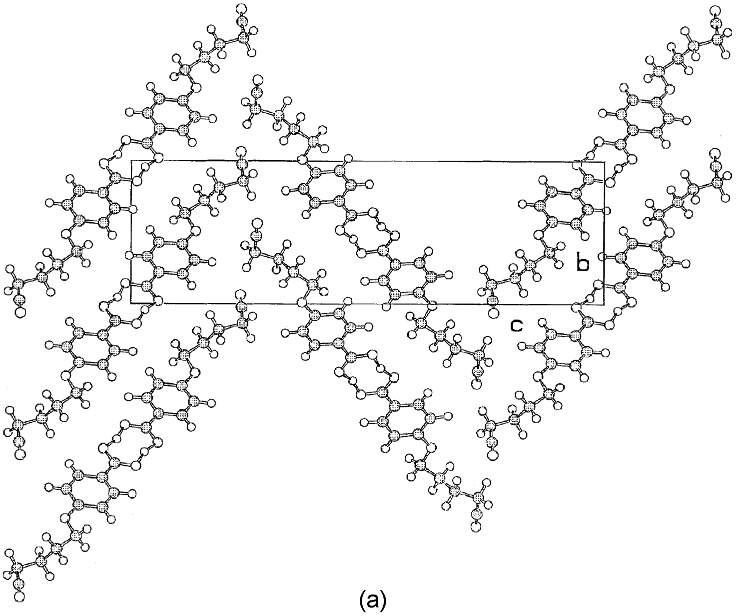


FIGURE 2 Representation of packing arrangements of CN4BS in (a) [100] projection, (b) [001] projection.

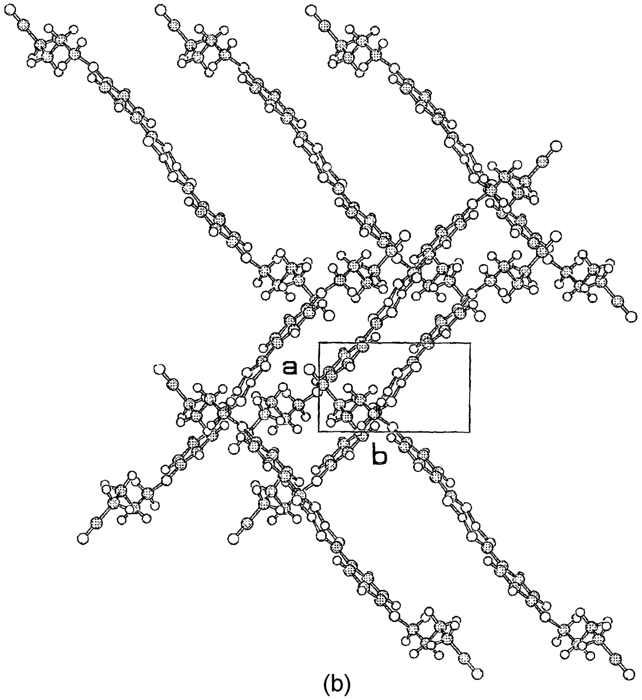


FIGURE 2 (*Continued.*)

figure. The maximum N..N distance amounts to ca. 4.0 Å, but due to a disordered cyano position, best described by partial occupancy, this distance might be in the range of a significant dipole-dipole interaction. The molecules of a string shifted in **b** direction form a plane shown in Figure 3(b). The maximum N..N distance of adjacent molecules of different strings shifted in **b** direction is 4.2 Å in the above-discussed disordered cyano terminal region but might be considerably less. It can be concluded from these distances that strong polar interactions exist along each string and also with the adjacent string shifted in **b** involving the terminal cyano sites. The adjacent strings in Figure 3(a) run perpendicular to each other, if the projection of the core of the molecules in the **b-c** plane is considered as demonstrated in Figure 3(c), and both strings are embedded in planes of similar running molecules in **b** direction. Only van der Waals contacts are present between these two neighboring planes.

Despite the similarity of the pattern in Figures 3(a) and 4(a) for the two compounds CN5BS and CN6BS, a distinct difference is present in the packing arrangement of CN6BS. The molecular backbone for CN5BS of the dimers in one string point in the same direction. The dimers of CN6BS form a zigzag string as shown in Figure 4(b) and adjacent dimers (cf. Figure 4(a), the ones with largest overlap) are placed in perpendicular directions. The strings along **b** are embedded in planes which interact by van der Waals forces. The terminal CN group of one CN6BS molecule interacts with the two adjacent ones and exhibits the same N..N distance of 4.01 Å (cf. Figure 4(b)).

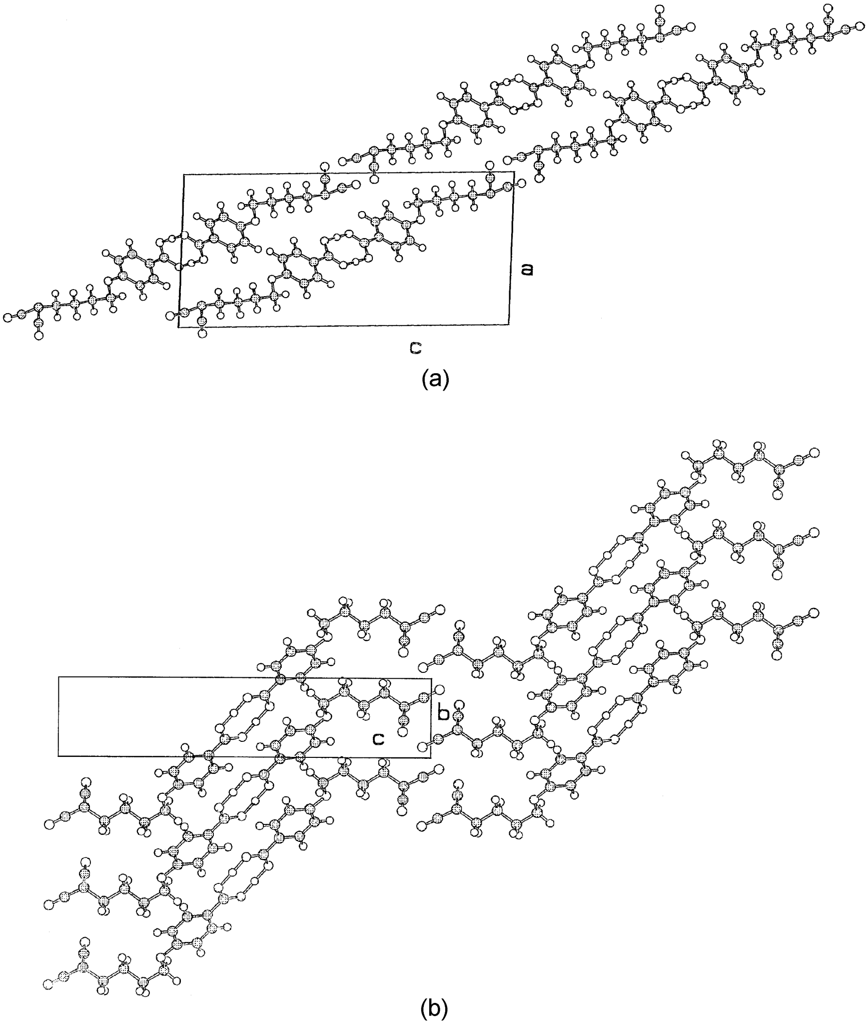


FIGURE 3 Representation of packing arrangements of CN5BS in (a) [010] projection, (b) [100] projection, and (c) perpendicular to the plane of the benzoic acid.

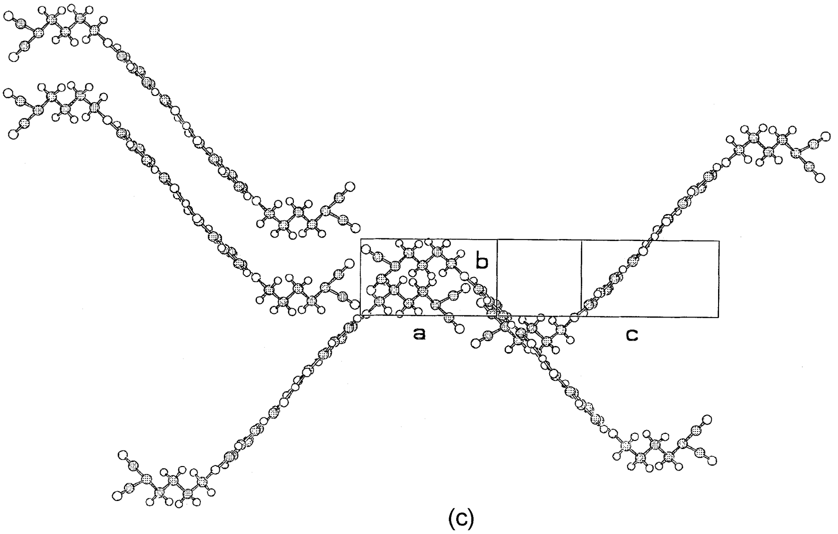


FIGURE 3 (*Continued.*)

The mixed compound CN4–5BS shows a herringbone packing arrangement projected in direction of the shortest unit cell axis [100] similar to CN4BS, as represented in Figure 5(a). However, differences are evident in projections on the **a-c** and **a-b** planes (Figure 5(b) and 5(c)). A uniform direction of the molecule backbone appears in the **a-c** plane in contrast to the **a-b** plane for CN4BS (Figure 2(b)) and the alkoxy group

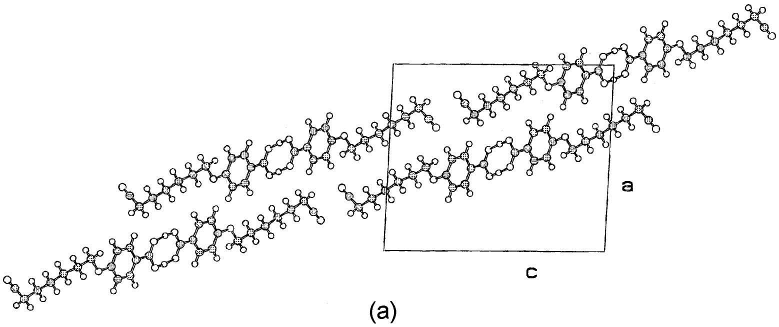


FIGURE 4 Representation of packing arrangements of CN6BS in (a) [010] projection, (b) [100] projection.

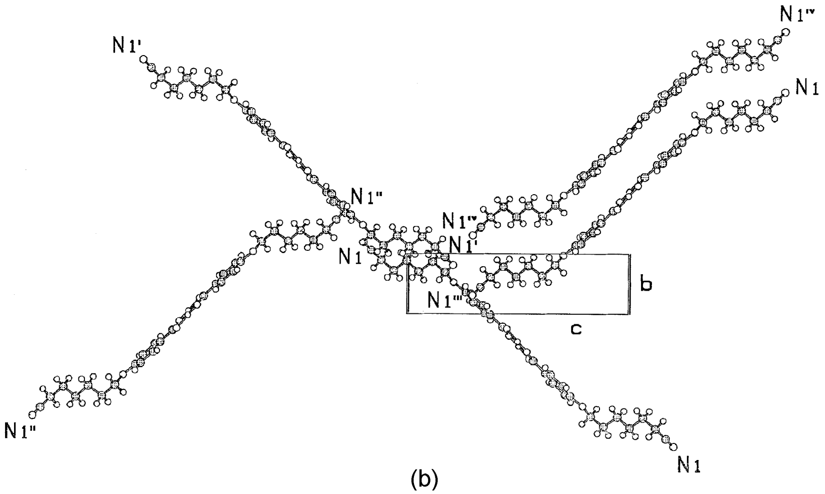


FIGURE 4 (*Continued.*)

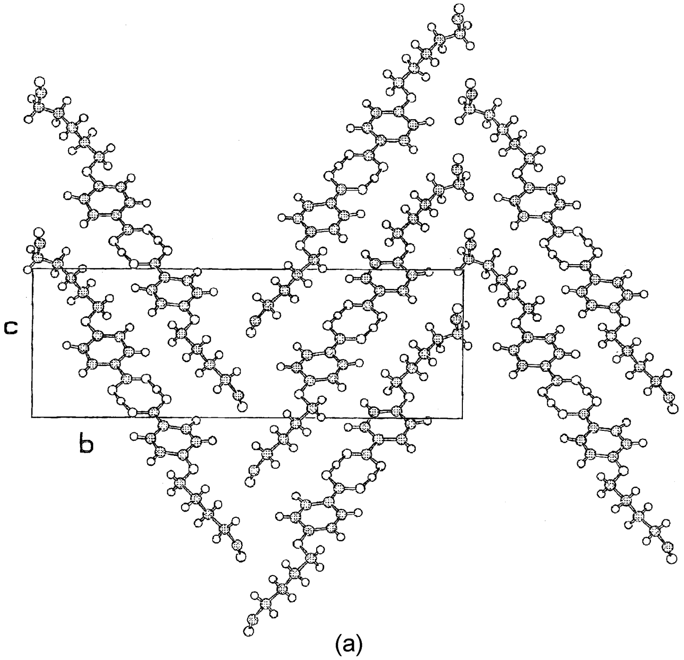
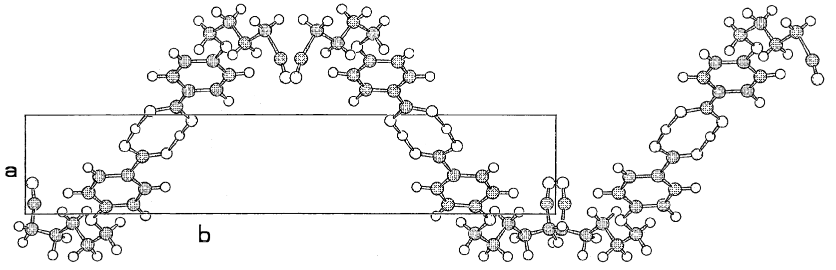
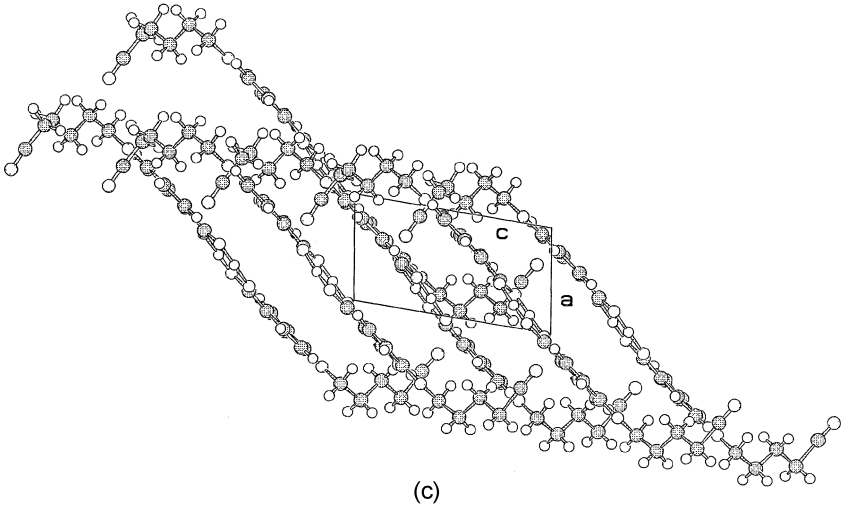


FIGURE 5 Representation of packing arrangements of CN4-5BS in (a) [100] projection, (b) [001] projection, and (c) [010] projection.



(b)



(c)

FIGURE 5 (*Continued.*)

of the shifted molecule along **a** appears at the center of the respective molecule. Strings cannot be defined, since the terminal cyano groups are placed in the interstitial spaces of the two molecules in opposite direction of the herringbone arrangement and in contact with the alkoxy chains of the same length (Figure 5(a)). The terminal N..N distances amount to 4.67 Å for contacts between CN5BS molecules, 4.64 Å for contacts between CN4BS molecules, and 4.96 Å for contacts between CN4BS and CN5BS molecules. In the projection on the **a-b** plane it appears that the terminal cyano groups are close and avoiding each other, but as discussed the distances between the terminal N atoms are too far apart to interact strongly.

TABLE 3 Hydrogen Bonds and Carbon-Oxygen Bond Distances Involving the Carboxylic Acid for CN4BS, CN5BS, CN6BS, and CN4–5BS

CN4BS									
C1–O1	1.263(2)	O1..O2′	2.620(2)	O1	1.30	H1O	1.36	O2′	161.5°
C1–O2	1.277(2)								
CN5BS									
C1–O1	1.244(3)	O1..O2′	2.629(3)	O1	1.31	H1O	1.32	O2′	179.9°
C1–O2	1.293(3)								
CN6BS									
C1–O1	1.301(4)	O1..O2′	2.641(4)	O1	1.17	H1O	1.47	O2′	175.2°
C1–O2	1.239(4)								
CN4–5BS									
C101–O101	1.303(6)	O101..O202	2.694(6)	O101	1.41	H11O	1.29	O202	172.5°
C201–O201	1.181(6)								
C101–O102	1.374(6)	O102..O201	2.566(6)	O102	1.20	H12O	1.37	O201	177.8°
C201–O202	1.275(6)								

Carbon-oxygen and oxygen-oxygen distances are listed in Å as well as those involving the attached hydrogen, and the corresponding angles are given in degrees.

Discussion

The different arrangements in molecular packing are reflected in the liquid crystalline behavior described by Bock [2]. CN4BS exhibits a crystalline phase which melts at 144.8°C. In contrast, CN5BS shows the

TABLE 4 Selected Torsion Angles of the Alkoxy Chain in Degree

	CN4BS	CN5BS	CN6BS	CN4–5BS	
τ(O3-C8-C9-C10)	66.5 (0.2)	−63.6 (0.3)	66.4 (0.4)	−66.1 (0.6)[#]	64.6 (0.5)§
τ(C8-C9-C10-C11)	−161.3 (0.1)	177.9 (0.2)	−178.1 (0.3)	178.7 (0.5)[#]	176.9 (0.5)§
τ(C9-C10-C11-C12)	−64.0 (0.2)	−174.2 (0.2)	175.2 (0.3)	−179.0 (0.5)[#]	139.0 (0.9)§
τ(C10-C11-C12-C13)		−59.3 (0.4)	179.4 (0.3)		72.5 (1.0)§
τ(C10-C11-C12-C13A)*		−162.2 (0.6)			
τ(C11-C12-C13-C14)			−65.9 (0.5)		

*Partial occupancy of C13A in CN5BS 25% and 75% for C13.

[#] CN4BS.

§CN5BS.

The sign of all torsion angles for one molecule is reversed, if the corresponding symmetry related molecule is considered.

following phase sequence: Cr1 83.2 Cr2 119.2 SmA 135.5 N 140.1 Is at heating and Is 142.3 N 136 SmA 83.6 Cr at cooling. CN6BS shows the following phase sequence: Cr 131.2 Is at heating and Is 124 SmX 74.8 Cr at cooling (temperatures in °C).

The dimeric arrangements of CN5BS with strong dipolar interaction in a continuous string leads to smectic and nematic phases at heating and cooling. X-ray measurements show a reflection at 35 Å in the smectic phase, which confirms existing dimers in the liquid crystalline state. Perpendicular running strings of adjacent sheets have to be rotated to point in a uniform direction. Such a cooperative rotation of all strings in one sheet seems possible, since only van der Waals interactions are present between these sheets. In contrast, CN6BS with a zigzag string formation exhibits a transition from crystalline to the isotropic melt but a monotropic transition to at least one unidentified smectic phase. The X-ray reflections of these phases lie at about 11.4 Å, which corresponds to the distance between two equivalent sheets (twice the van der Waals distance of adjacent sheets) in the crystalline state represented by a strong (101) reflection. The kind of smectic phase could not be determined. The length of the dimers does not appear in the X-ray pattern. On the other side, molecules such as CN4BS with no string formation do not form any liquid crystals. The characterization of CN4-5BS was not carried out due to the lack of a sufficient amount this special substance.

CONCLUSION

The idea that dimers represent the basic units in benzoic acids in the crystalline state was confirmed [1]. However, the dimers cannot be regarded as the basic entity of the nucleation process already formed in solution. It is unlikely that by dissolving a 1:1 mixture of CN4BS and CN5BS a 1:1 compound is formed in solution, rather that a rearrangement occurs during nucleation which implies a breaking of hydrogen bonds and new arrangements of molecules during crystallization. If only the randomly occurring 1:1 compounds crystallize, CN4BS and CN5BS crystals should be formed also but in actuallity are not found. It is interesting to note that if the strong dipolar interaction by hydrogen bonds at the carboxylic acid sites of the molecules is compensated in a small volume fraction of the unit cell leading to low energy density, there is no need for nonenantiomeric molecules to crystallize in a centrosymmetric space group; rather a good or even better packing arrangement may occur in noncentrosymmetric or in optical-active space groups [7]. The density of the 1:1 aggregate compares with that of CN4BS, which lies above the expected average density by CN4BS and CN5BS crystals and supports this idea.

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