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Peter Zugenmaier[a]
[a] Institut für Physikalische Chemie der TU Clausthal, D-38678 Clausthal-Zellerfeld, Germany

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Crystal and molecular structures of four model compounds for liquid crystal dimers with a methylene spacer of various lengths

PETER ZUGENMAIER
Institut für Physikalische Chemie der TU Clausthal, Arnold-Sommerfeld-Str. 4, D-38678 Clausthal-Zellerfeld, Germany

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The crystal and molecular structures of four model compounds for liquid crystal dimers namely, 4,4-[octyl]bis-acetophenone (B(AcP)8), 4,4-[heptyl]bis-acetophenone (B(AcP)7), 4,4-[hexyl]bis-acetophenone (B(AcP)6), and 1,1-(1,6-hexyldion)bis-benzene (DP6D), have been determined in order to gain an insight into observed differences in the textures of liquid crystalline phases of compounds with odd and even methylene spacers. All four compounds exhibit extended conformations with an all-*trans* conformation of the methylene chain but a twist between phenyl rings of about 125°, except DP6D for which the benzene groups lie in plane with the methylene chain. Half a molecule is necessary to represent the asymmetric unit of compounds with even numbers *n* of methylene groups in the spacer and belong to centrosymmetric space groups. The model compound with an odd value of *n* is non-centrosymmetric and shows another type of packing arrangement which may cause different textures and behaviour for dimesogenic compounds in the liquid crystalline state.

1. Introduction

In previous studies the conformations and arrangements of dimeric compounds with methylene and dimethylsiloxane spacers linking two biphenyl semi-rigid units of various types were investigated by single crystal analysis, and it was shown that the methylene spacers exhibit an extended rod-like form [1–4], even when *gauche* conformations are present. In contrast, the dimethylsiloxane spacer forms a loop or fold [5]. The molecular conformation is then also a hairpin (in the liquid crystalline state) due also to the dimethylsiloxane groups, while the conformation of methylene spaces remains linear or rod-like [6]. Dimesogenic compounds with even and odd numbers of methylene spacer groups show different textures in the liquid crystalline state that may be caused by differences in the packing of the molecules. Therefore, an investigation has been undertaken to study the conformation and arrangements of model compounds for the dimers, but which are not dimesogenic themselves. The required information can be obtained for these compounds in the crystalline state by single crystal studies in which the shape and packing may easily be determined. The use of model compounds is often necessary in these investigations since the liquid crystal dimesogenic compounds, and in particular those with odd numbers of methylene groups, often crystallize poorly. We do note, however, that the insights gained using these model compounds should only be extended to the liquid crystalline materials with some reservations.

2. Structure solution and refinement

Single crystals of the compounds suitable for X-ray determination were provided by Dr Thyen [7]. Data collection was performed on a CAD4 instrument with MoK_α radiation and the MoLEN package of Enraf Nonius Delft [8] was used for data processing and refinement against *F*. The hydrogen atoms were placed at respective sites and not refined as well as their isotropic *B* values. Tables 1 and 2 represent the basic crystallographic data and tables 3–6 the fractional coordinates of the asymmetric unit. The figures for the representation of conformation and packing were produced with SCHAKAL 92 [9].

3. Results and discussion

3.1. *Molecular geometry and conformation*

Figure 1 shows the molecular geometry and atom labelling of the four structures: 4,4-[octyl]bis-acetophenone (B(AcP)8), 4,4-[heptyl]bis-acetophenone (B(AcP)7), 4,4-[hexyl]bis-acetophenone (B(AcP)6), 1,1-(1,6-hexyldion)-bis-benzene (DP6D). Half a molecule suffices as the

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Corresponding author.
Email: Zugenmaier@pc.tu-clausthal.de

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Table 1. Summary of crystallographic data of 4,4-[octyl]bis-acetophenone, B(AcP)8 and 4,4-[hexyl]bis-acetophenone B(AcP)6. Estimated standard deviations in parenthesis.

Parameter	B(AcP) 6	B(AcP) 8
Molecular formula	C22 H26 O2/2	C24 H30 O2/2
Formula weight g mol^{-1}	322.45/2	350.50/2
Crystal system	monoclinic	monoclinic
Space group	$C\ 2/c$ (15)	$C\ 2/c$ (15)
a Å	23.284(7)	23.825(6)
b Å	5.4555(6)	5.3776(3)
c Å	15.836(4)	17.194(4)
α °	90	90
β °	114.23(1)	110.33(1)
γ °	90	90
VÅ^3	1834.3(8)	2065.7(7)
Z	4 × 2	4 × 2
D_{cal} g cm^{-3}	1.17	1.13
μ(MoK$_\alpha$) cm^{-1}	0.7	0.7
λ(MoK$_\alpha$) Å	0.71073	0.71073
Number of reflections for lattice refinement	25	25
Scan range in θ °	10–25	9–20
Reflections collected	1180	1964
Unique data	1124	1880
Data collection (<θ<)	1–22	1–25
$I_0 > 3\sigma$	791	1026
Parameters refined	109	118
F(000)	696	760
R	0.045	0.059
R_{w}	0.059	0.073
Highest peak e Å^{-3}	0.14(3)	0.20(6)
Crystal colour	colourless	colourless
Crystal size mm^3	parallelepiped (0.6 × 0.4 × 0.2)	parallelepiped (0.7 × 0.55 × 0.3)

Table 2. Summary of crystallographic data of 4,4-[heptyl]bis-acetophenone, B(AcP)7, and 1,1-(1,6-hexyldion)bis-benzene, DP6D.

Parameter	B(AcP) 7	DP6D
Molecular formula	C23 H28 O2	C18 H18 O2/2
Formula weight g mol^{-1}	336.42	266.34/2
Crystal system	monoclinic	triclinic
Space group	$P\ n$ (7)	$P{-}1$ (2)
a Å	5.706(1)	5.728(2)
b Å	30.377(4)	7.837(3)
c Å	5.707(1)	8.410(3)
α °	90	95.84(2)
β °	98.40(1)	105.61(2)
γ °	90	95.89(2)
V Å^3	978.7(3)	358.2(3)
Z	2	1 × 2
D_{cal} g cm^{-3}	1.14	1.23
μ(MoK$_\alpha$) cm^{-1}	0.7	0.7
λ(MoK$_\alpha$) Å	0.71073	0.71073
Number of reflections for lattice refinement	25	25
Scan range in θ °	9–17	8–23
Reflections collected	1357	1396
Unique data	1355	1256
Data collection (<θ<)	1–22	1–25
$I_0 > 3\sigma$	937	883
Parameters refined	224	91
F(000)	364	142
R	0.041	0.044
R_{w}	0.050	0.063
Highest peak e Å^{-3}	0.11(3)	0.19(3)
Crystal colour	colourless	colourless
Crystal size mm^3	platelet (0.6 × 0.6 × 0.15)	platelet (0.7 × 0.3 × 0.09)

asymmetric unit for the observed centrosymmetric space groups since the other half is reproduced by an inversion centre in the middle of the even numbered methylene chain. The dimers, α,ω-bis[4-(4′-hexyloxy- or heptyloxy-benzylideneiminophenyl)]octane (6O.8.O6 or 7O.8.O7), with an even number of methylene groups n in the spacer which exhibit crystalline, G and nematic phases, also crystallize in a centrosymmetric space group with the inversion centre in the middle of the molecule [4]. However, α,ω-bis[4-(4′-butyloxy- or pentyloxy-benzylideneiminophenyl)]octane (4O.8.O4 or 5O.8.O5) possess a centre of symmetry between the chains [3], and the whole molecule serves as an asymmetric unit. In contrast, the molecule with an odd number of methylene groups B(AcP)7 crystallizes in a non-centrosymmetric space group. The molecule is bent as shown in figure 1 (d), which has consequences for the packing arrangements to be discussed later. The bonds of the alkane chains in all four compounds

Table 3. Fractional coordinates and isotropic displacement parameters B_{eq} of 4,4-[octyl]bis-acetophenone, B(AcP)8. Estimated standard deviations in parenthesis.

Atom	x	y	z	B_{eq}/Å^2
O1	0.32480(9)	0.1950(4)	−0.1461(1)	10.24(6)
C1	0.2724(1)	0.5592(6)	−0.1388(2)	8.45(8)
C2	0.3120(1)	0.3418(5)	−0.1019(1)	6.97(7)
C3	0.33498(9)	0.3075(4)	−0.0106(1)	5.90(6)
C4	0.3735(1)	0.1138(5)	0.0241(2)	7.26(7)
C5	0.3951(1)	0.0715(5)	0.1077(2)	7.38(7)
C6	0.3790(1)	0.2206(5)	0.1615(1)	6.52(6)
C7	0.3409(1)	0.4170(5)	0.1274(1)	7.66(7)
C8	0.3192(1)	0.4585(5)	0.0431(2)	7.18(7)
C9	0.4012(1)	0.1706(5)	0.2533(2)	7.93(8)
C10	0.4355(1)	0.3812(5)	0.3071(1)	6.76(6)
C11	0.4549(1)	0.3253(5)	0.3990(1)	6.72(6)
C12	0.4913(1)	0.5279(5)	0.4543(1)	6.58(6)

Table 4. Fractional coordinates and isotropic displacement parameters B_{eq} of 4,4-[hexyl]bis-acetophenone, B(AcP)6. Estimated standard deviations in parenthesis.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
O1	0.32574(9)	0.1743(4)	−0.1331(1)	8.88(6)
C1	0.2704(1)	0.5333(5)	−0.1328(2)	6.54(8)
C2	0.3134(1)	0.3253(5)	−0.0870(2)	5.73(7)
C3	0.3402(1)	0.3011(4)	0.0158(2)	4.80(6)
C4	0.3801(1)	0.1082(5)	0.0582(2)	5.77(7)
C5	0.4061(1)	0.0807(5)	0.1528(2)	5.84(7)
C6	0.3928(1)	0.2451(5)	0.2091(2)	5.24(6)
C7	0.3529(1)	0.4392(5)	0.1669(2)	5.82(7)
C8	0.3271(1)	0.4663(5)	0.0720(2)	5.47(6)
C9	0.4197(1)	0.2148(5)	0.3131(2)	6.14(7)
C10	0.4577(1)	0.4308(5)	0.3680(2)	5.58(7)
C11	0.4809(1)	0.3946(4)	0.4715(2)	5.61(7)

Table 5. Fractional coordinates and isotropic displacement parameters B_{eq} of 1,1-(1,6-hexyldion)bis-benzene, DP6D. Estimated standard deviations in parenthesis.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
O1	1.0795(2)	0.7310(2)	0.7117(2)	6.08(3)
C1	1.2052(4)	0.8763(3)	1.3196(2)	5.98(5)
C2	0.9770(4)	0.7790(3)	1.2562(2)	6.18(5)
C3	0.8907(3)	0.7194(3)	1.0880(2)	5.17(4)
C4	1.0312(3)	0.7548(2)	0.9816(2)	4.01(4)
C5	1.2612(3)	0.8505(3)	1.0480(2)	4.89(4)
C6	1.3468(4)	0.9109(3)	1.2163(2)	5.75(5)
C7	0.9453(3)	0.6973(2)	0.7977(2)	4.21(4)
C8	0.6934(3)	0.5985(2)	0.7227(2)	4.45(4)
C9	0.6245(3)	0.5543(3)	0.5350(2)	4.59(4)

Table 6. Fractional coordinates and isotropic displacement parameters B_{eq} of 4,4-[heptyl]bis-acetophenone, B(AcP)7. Estimated standard deviations in parenthesis.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
O1	−0.3152(8)	0.0545(1)	−0.2048(6)	11.3(1)
O2	1.8035(7)	0.4456(1)	1.9167(8)	11.1(1)
C1	−0.281(1)	0.0240(2)	0.1761(8)	8.7(1)
C2	−0.207(1)	0.0544(1)	−0.0034(8)	7.5(1)
C3[a]	−0.001	0.0845(1)	0.0580	6.7(1)
C4	0.055(1)	0.1145(2)	−0.1030(7)	8.3(1)
C5	0.2422(9)	0.1433(2)	−0.0513(7)	8.5(1)
C6	0.3845(8)	0.1422(1)	0.1679(7)	7.3(1)
C7	0.330(1)	0.1119(1)	0.3294(7)	7.9(1)
C8	0.1411(9)	0.0835(1)	0.2768(7)	7.7(1)
C9	0.597(1)	0.1718(2)	0.2171(8)	8.6(1)
C10	0.6254(9)	0.1975(2)	0.4427(8)	7.6(1)
C11	0.8502(9)	0.2241(1)	0.4835(8)	7.5(1)
C12	0.8882(9)	0.2497(2)	0.7119(8)	8.0(1)
C13	1.1160(9)	0.2754(1)	0.7495(8)	7.4(1)
C14	1.1600(9)	0.3024(2)	0.9747(8)	7.8(1)
C15	1.3828(9)	0.3284(2)	1.0036(9)	8.7(1)
C16	1.4323(8)	0.3581(1)	1.2169(8)	7.3(1)
C17	1.6508(8)	0.3570(2)	1.3593(8)	8.5(1)
C18	1.7020(8)	0.3859(2)	1.5464(8)	8.5(1)
C19	1.5422(7)	0.4158(1)	1.6024(8)	6.6(1)
C20	1.3222(9)	0.4169(1)	1.4578(8)	7.7(1)
C21	1.2705(9)	0.3887(1)	1.2726(9)	7.9(1)
C22	1.6024(9)	0.4461(1)	1.8072(9)	7.5(1)
C23	1.423(1)	0.4759(2)	1.8802(9)	8.8(1)

[a]*x*, *z* coordinates fixed for space group *Pn*.

closely represent all-*trans* conformations, i.e. the skeleton of the chain lies almost in a plane. For DP6D this plane also contains the carbonyl groups and the benzene rings. For the other three compounds the benzene ring

Table 7. Selected torsion angles (°) and length of the molecule (Å). For corresponding angles for B(AcP)7 and DP6D see footnotes.

Angle	B(AcP) 8	B(AcP) 6	DP6D	B(AcP) 7
τ(C5–C6–C9–C10)	122.0 (3)	122.8 (3)	0.9 (3)	131.5 (5)
τ(C5′–C6′–C9′–C10′)	−122.0 (3)	−122.8 (3)	−178.1 (2)	130.8 (5)[a]
τ(C7–C6–C9–C10)	−59.0 (4)	−58.1 (4)	−0.9 (3)	−51.7 (7)
τ(C7′–C6′–C9′–C10′)	59.0 (4)	58.1 (4)	178.1 (2)	−52.6 (7)[b]
τ(C4–C3–C2–C1)	−177.2 (3)	−179.9 (3)		−175.1 (5)
τ(C4′–C3′–C2′–C1′)	177.2 (3)	179.9 (3)		−174.7 (5)[c]
τ(C5–C6..C6′–C5′)	−180.0 (3)	179.9 (3)	−180.0 (2)[g]	−139.4 (5)[d]
l(O1..O1′)	21.100	18.627	16.287[h]	19.778[e]
l(C1..C1′)	20.858	18.446	14.282	18.708[f]

[a]τ(C14–C15–C16–C17).
[b]τ(C14–C15–C16–C21).
[c]τ(C18–C19–C22–C23).
[d]τ(C5–C6–C16–C17).
[e]*l*(O1..O2).
[f]*l*(C1..C23).
[g]τ(C3–C4..C4′–C3′).
[h]*l*(H1..H1′).

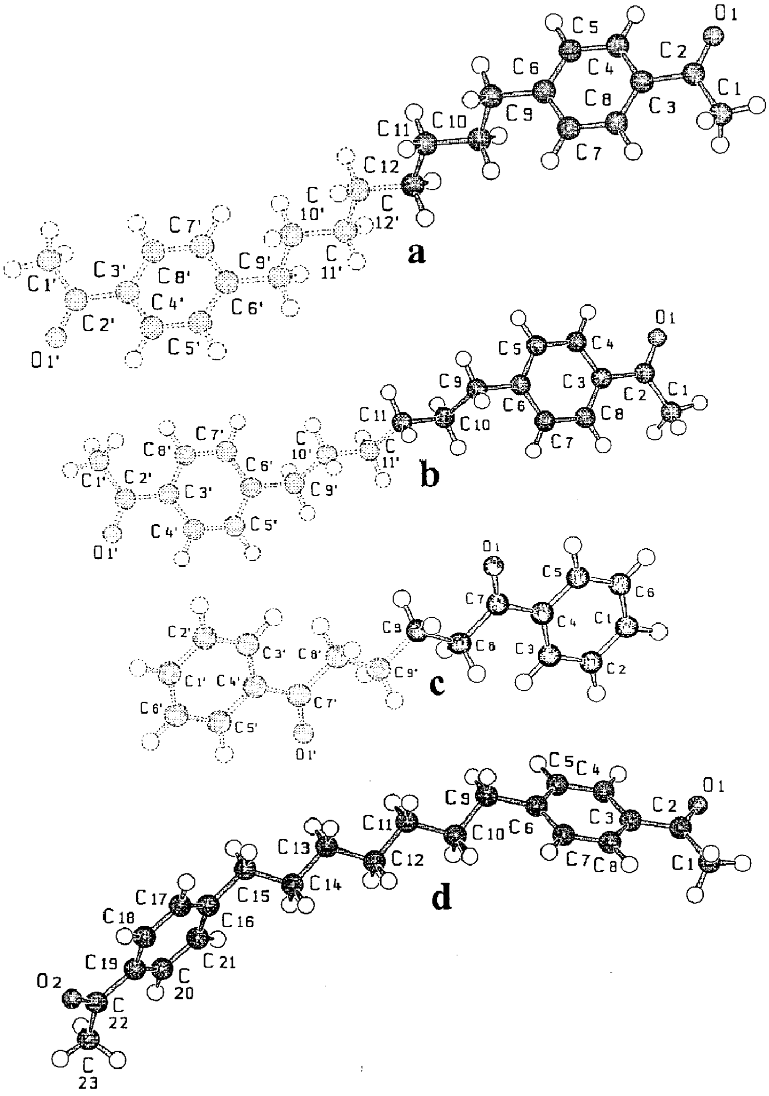

Figure 1. Representation of conformation and atom labelling of four model compounds: (*a*) 4,4-[octyl]bis-acetophenone B(AcP)8, (*b*) 4,4-[hexyl]bis-acetophenone B(AcP)6, (*c*) 1,1-(1,6-hexyldion)bis-benzene DP6D, (*d*) 4,4-[heptyl]bis-acetophenone B(AcP)7.

is twisted out of the methylene plane and can best be represented by the corresponding torsion angles listed in table 7.

The centre of inversion symmetry causes the torsion angles of the asymmetric unit, e.g. τ(C5–C6–C9–C10), to be reversed in sign in the second half of the molecule with the result that the twisting of the two benzene rings is cancelled: the two benzene rings are lying in a plane as demonstrated by a torsion angle of τ(C5–C6..C6′–C5′) of $\pm 180°$. The torsion angles of the benzene rings towards the methylene groups of the two compounds B(AcP)8 and B(AcP)6 are comparable, as are the almost planar positions of the two carbonyl groups associated with the benzene rings at the beginning and end of the two molecules (see table 7). This observation is also true for one end of B(AcP)7, however the twist is not reversed at the other end of the molecule but rather has the same sign, leading to a considerable bend of the molecule as shown in figure 1 (*d*). In a projection perpendicular to the one shown in figure 1 (*d*), the molecule appears rod-like and comparable to B(AcP)8 or B(AcP)6 (see figure 2). It is clear that this shape of the molecule will lead to a different packing arrangement, to be discussed later. The length of the molecules are obtained by adding the lengths of the various parts; the difference between the lengths of B(AcP)8 and B(AcP)6 agrees with the length of an ethylene unit in polyethylene or paraffin (see table 7).

The C–C distance in the methylene spacer is about 0.03 Å shorter than the average experimentally

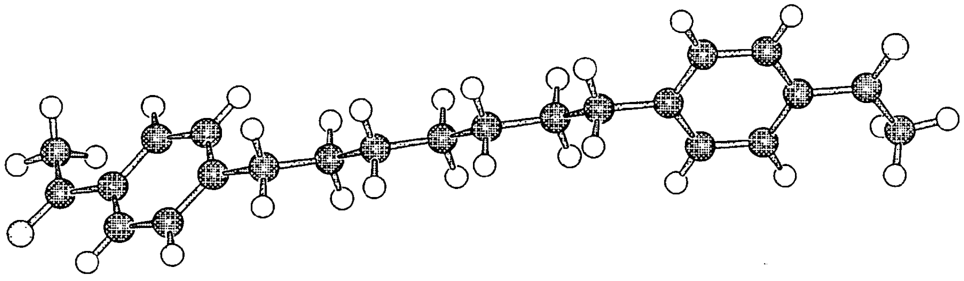

Figure 2. Representation of 4,4-[heptyl]bis-acetophenone, cf. figure 1(*d*), in another projection showing an almost straight molecular shape.

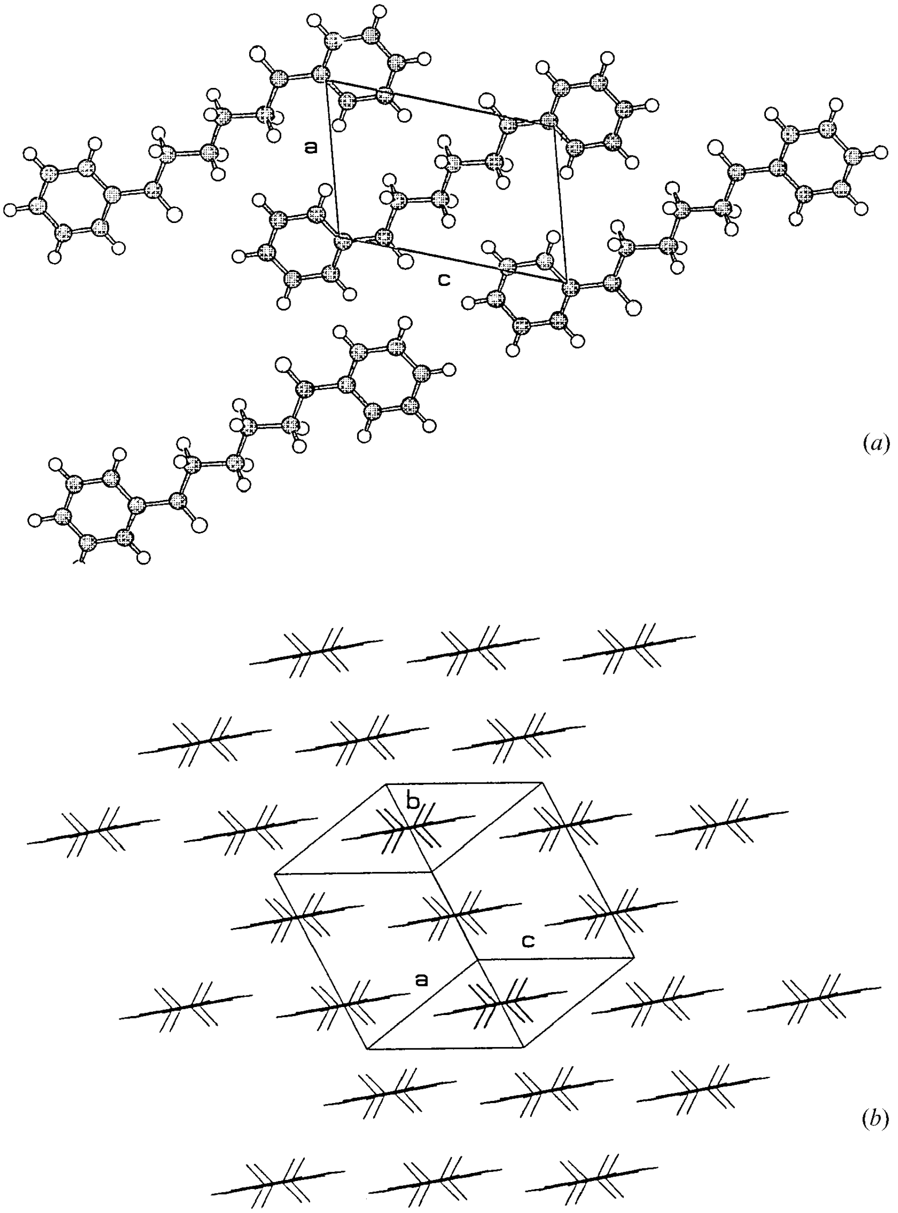

Figure 3. Representation of packing arrangements of 1,1-(1,6-hexyldion)bis-benzene DP6D in two projections: (*a*) projection on the *ac*-plane; (*b*) projection down the molecular axes. Note the almost perfect orientation of the planar molecules forming strings of succeeding molecules.

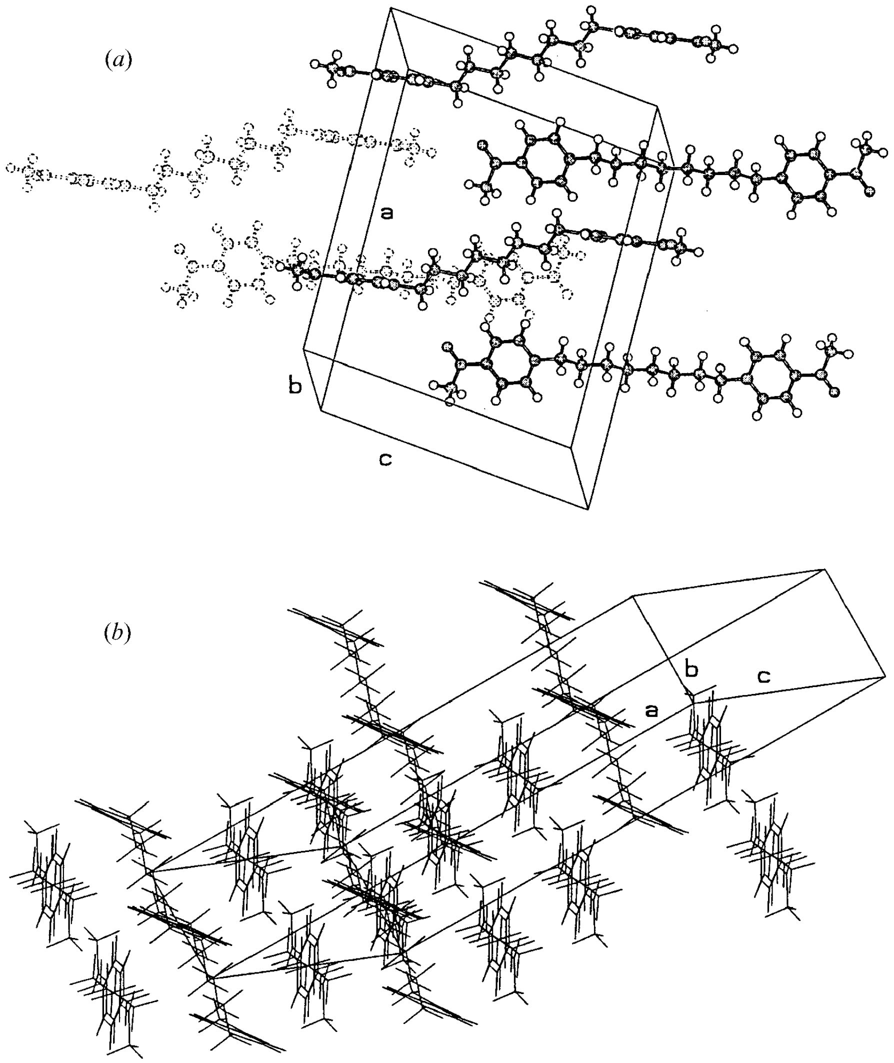

Figure 4. Representation of packing arrangements of 4,4-[octyl]bis-acetophenone B(AcP)8 in two projections. (*a*) Projection showing two pairs of the four molecules of the unit cell in different spatial positions. Two succeeding molecules, of which one is represented in light drawing, are in different spatial position as well as the adjacent molecule placed below. (*b*) Projection representing the different orientation of the molecules which does not lead to an overlap of axes of strings and of molecules as shown in figure 3 (*b*).

established CCDC value and the bond angles in the methylene chain are a little larger than expected, but both angles and bonds agree with those of similar compounds [3, 4]. The deviations from the standard values may be due to high thermal motion.

3.2. *Packing arrangements*

Three of the four structures investigated belong to centrosymmetric space groups; two, B(AcP)6 and B(AcP)8, belong to the identical space group *C*2/*c* and are very similar in the size of the cell parameter (elongation in one dimension by an ethylene group) and consequently in molecular arrangements. DP6D belonging to $P-1$ shows a somewhat different packing arrangement. In contrast B(AcP)7 with an odd number of methylene groups exhibits a non-centrosymmetric space group *Pn* and a different kind of packing arrangement. Since the packing of B(AcP)6 and B(AcP)8 are similar, with just an elongation of the molecule by an ethylene group, only one of the packing arrangements of these structures will be discussed. DP6D exhibits a simple packing arrangement, as shown in figure 3, and can be described by stapled planes in which the molecules are placed approximately in line, thus forming strings. The flat molecules with the centre lying on an inversion centre are slightly tilted out of the depicted plane, figure 3 (*a*). A projection down the

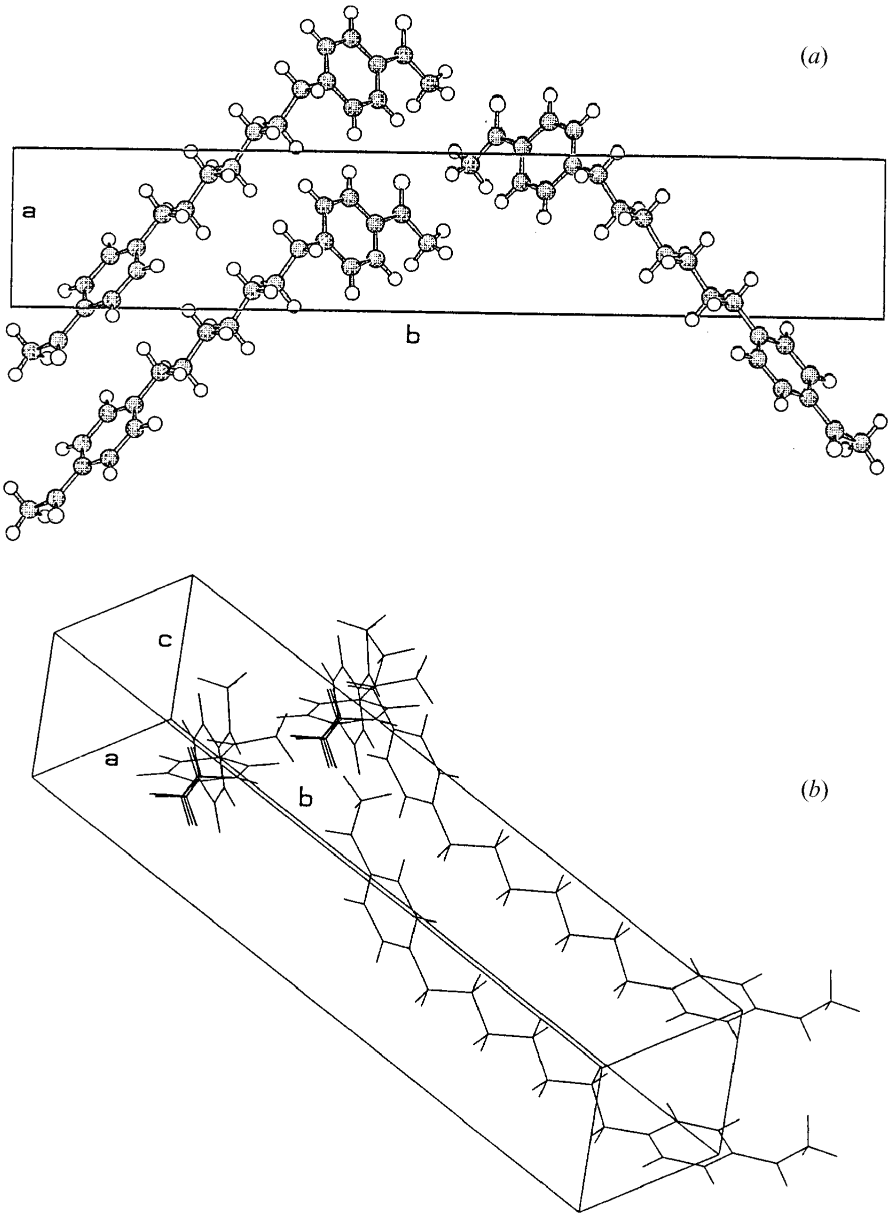

Figure 5. Representation of packing arrangements of 4,4-[heptyl]bis-acetophenone B(AcP)7 in two projections. (*a*) Projection of four molecules on the *ab*-plane showing a herringbone arrangement; one of the molecules is completely overlapped. The same arrangement is obtained in projection on the *cb*-plane. (*b*) Projection down the methylene backbone of two molecules of figure 5 (*a*). No uniform projection of all four molecules can be achieved as in figure 3 (*b*).

rod-like molecule, figure 3 (*b*), shows the perfect orientation of the string forming molecules. Figure 4 shows the packing of B(AcP)8. The projected molecules in figure 4 (*a*) are twisted in two different spatial arrangements and the strings formed consist of two differently twisted and bent molecules. The axes of the string-forming molecules do not coincide with the axes of the individual molecules but rather have to be considered as an average of two differently oriented, succeeding molecules with dissimilar spatial axes; the benzene rings protrude from the projected methylene groups, figure 4 (*b*). All the centres of individual molecules are coincident with inversion centres.

The packing of B(AcP)7 in a non-centrosymmetric space group *Pn* can be described as a herringbone arrangement and the strings of succeeding molecules follow a zigzag shape. Figure 5 (*a*) shows the projection of the molecules on the *ab*-plane. The projection of the molecules on the *cb*-plane leads to exactly the same pattern. The equivalence of the two projections is also demonstrated by the same values of the cell parameters *c* and *a*. If the molecules pointing in one direction are projected down the methylene axis, the molecules pointing in the other direction are lying almost in the perpendicular direction, figure 5 (*b*).

4. Conclusions

It was seen that the carbonyl bond lies coplanar with adjacent atoms, i.e. in the benzene plane, for all the structures solved and additionally in the methylene plane for DP6D. Therefore, DP6D is a planar molecule. For the other three structures the bond C9–H9(A or B) is coplanar with the benzene ring, allowing two possible sites for the benzene ring depending on symmetry relationships and/or packing arrangements. Thus the benzene ring is twisted out of the methylene plane by about $\pm 58^\circ$ for B(AcP)8 and B(AcP)6, depending on the reference hydrogen atom (H9A or H9B). Only one twisting sense of about 52° occurs for B(AcP)7.

The compounds investigated may serve as models for dimesogenic molecules which exhibit liquid crystalline phases in as much as the methylene spacers exhibit an all-*trans* conformation as found in this study in the crystal phase, and also as implied from the results of small angle X-ray investigations in the liquid crystalline state [3, 4, 6]. In contrast the siloxane spacer is more flexible causing a hairpin shape of the molecule detected in a single crystal study and in the liquid crystalline state [5, 10].

The packing arrangements of the crystal structures for odd and even numbers of methylene groups differ considerably: linear arrangements of molecules with even-numbered spacers, but herringbone arrangements for odd numbered spacers; but they also differ in the basic symmetry elements of the space group, centrosymmetry for even *n* and no centre of symmetry for odd *n*. For the crystalline dimesogenic compound 5.O*n*O.5 with a methylene spacer $n=4$, a centrosymmetric space group $P-1$ was found, but with an odd methylene spacer $n=5$ an enantiomeric space group $P2_1$ was found, with the five methylene groups in all-*trans* conformation [1]. The different symmetry of the crystalline arrangements seems to be carried over to the liquid crystalline state causing different textures of the dimesogenic compounds with odd and even-numbered methylene spacers [6].

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