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Peter Zugenmaier

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Hairpin conformation of a chiral siloxane-based dimesogenic compound by single crystal analysis

PETER ZUGENMAIER*

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

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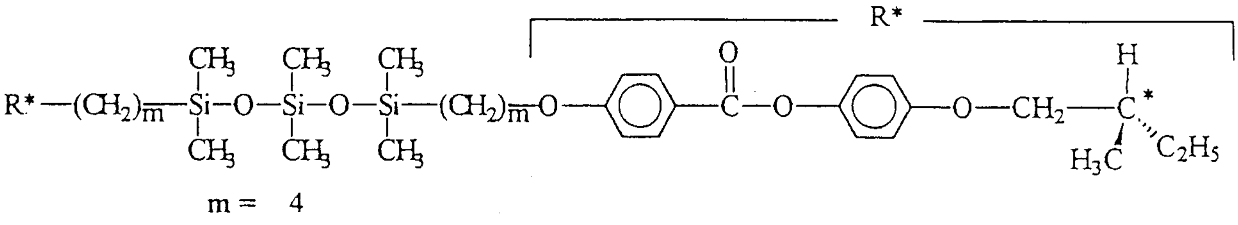
A hairpin conformation of a siloxane-based dimesogen was established on atomic resolution by evaluation of a single crystal structure and the fold described by bond lengths and bond angles, as well as by torsion angles. This hairpin conformation can be extended in the crystalline and liquid crystalline states to a homologous series of dimesogenic compounds with a hexamethyltrisiloxane unit connecting the two mesogenic parts of the molecules.

1. Introduction

A homologous series of dimesogenic compounds based on 4-(2-methylbutyloxy)phenyl-4-alkenyloxybenzoates and a hexamethyltrisiloxane unit has been synthesized in both chiral and racemic forms, characterized and investigated in the liquid crystalline and crystalline states by several methods [1, 2]. Small angle X-ray analysis gives reflections corresponding to one half of the molecular length for all of the materials in the liquid crystalline state and a study of a single crystal allowed us to propose on sound grounds that a hairpin conformation is present in these structures. We succeeded in crystallizing a second chiral dimesogenic compound (−)4Dim (*cf.* the scheme below) and obtained just enough X-ray data to solve the structure at a reasonably defined approximation on atomic resolution, which is justified by the good quality of fit, as well as by the temperature and disorder factors.

2. Experimental, structure solution and refinement

Crystals of (−)4Dim, suitable for an X-ray determination, were obtained by slow crystallization from solutions in a mixture of light petroleum/methylene chloride at low temperatures. Data collection was performed on a CAD4 single crystal diffractometer, with MoK_α radiation and data processing and refinement against *F* with the MolEN package of Enraf Nonius, Delft [3]. The starting model was produced by SIR 97 in space group *P*1 [4]. Because of the limited number of X-ray reflections only an isotropic refinement was undertaken except for the Si atoms, their adjacent O atoms and their pendant methyl carbons which were refined anisotropically. Further, it was discovered that the two molecules present in space group *P*1 are related by an inversion symmetry element, except for the chiral terminal groups which anyhow were difficult to locate because of high temperature factors. Therefore, the refinement was performed in space group *P*-1 to reduce the number of parameters. This procedure, which represents an approximation, is also justified by the result and will be discussed later. Table 1 shows the basic crystallographic data with the number of reflections adjusted to space group *P*-1. The pendant C22B atom of Si22 (*cf.* figure 1) was treated as a riding atom because of correlation problems during refinement. The figures representing the conformation and packing of the structures were produced with SCHAKAL 92 [5].



Scheme.

*Author for correspondence, e-mail: Zugenmaier@pc.tu-clausthal.de

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Table 1. Summary of crystallographic data for (−)4Dim.

Parameter	Value
Molecular formula	$C_{50}H_{72}Si_3O_{10}$
Formula mass	917.38
Crystal system	triclinic
Space group (Int. Tables)	*P* 1 (1) approx. *P*-1 (2)
a/Å	11.281 (5)
b/Å	11.429 (4)
c/Å	21.962 (9)
α/°	101.17 (2)
β/°	97.22 (2)
γ/°	92.75 (2)
V/Å^3	2747 (2)
Z	2
D_{cal}/g cm^{-3}	1.11
μ (MoK$_\alpha$)/cm^{-1}	1.3
λ (MoK$_\alpha$)/Å	0.71073
Number of reflections (lattice refinement)	25
Scan range in θ/°	5–11
Reflections collected	10188
Unique data	5095
Data collection [° < θ < °]	1–20
$I_0 > 2\sigma$	1620
Parameters refined	303
F(0 0 0)	988
R	0.135
R_w	0.159
Highest peak/e Å^{-3}	0.32(8)
Crystal colour	turbid
Crystal size/mm^3	0.25 × 0.35 × 0.45

3. Results and discussion

3.1. *Molecular geometry and conformation*

Figure 1 represents the molecular geometry and atom labelling of a single hairpin conformation. Due to a limited number of reflections, the refinement was carried out with isotropic temperature factors, only the heavy Si atoms, their adjacent oxygen and methyl carbon atoms were refined anisotropically. The hydrogen atoms were omitted. The result of this refinement is presented in table 2 in which the fractional coordinates are collected. The refinement was carried out in space group *P*-1 as an approximation, since it was found that when space group *P*1 is applied, the two terminal enantiomeric groups exhibit very high temperature or disorder factors caused by rotational mobility of the groups. This means that these groups are in various rotational positions with partial occupancy, which can be described to a certain approximation by space group *P*-1 with a small increase in temperature factors which does not influence greatly the rest of the molecule; this obeys space group *P*-1 as deduced from the comparable positions of atoms of the two molecules in the space group *P*1 of the unit cell. The justification for this approximation is further supported by the fact that the benzene rings have excellent planar geometry, and the temperature factors of the atoms lie in the expected range. High mobility causes higher temperature factors for some atoms, but this observation is not restricted to space group *P*-1, occurring also when refined in space group *P*1. The lack of data leads to a very imprecise structure in space group *P*1; but the structure improves in space group *P*-1, as detected by a narrower distribution of bond lengths and angles around the expected standard values. The coordinates of the atoms calculated in space group *P*-1 compare within the expected limits with those of one of the molecules derived in space group *P*1. It should be emphasized that the data are not as precise as in single crystal studies with a good parameter to reflections ratio, but the data clearly support a hairpin conformation and describe a short and sharp siloxane fold in terms of standard bond lengths and angles, as well as torsion angles on atomic resolution.

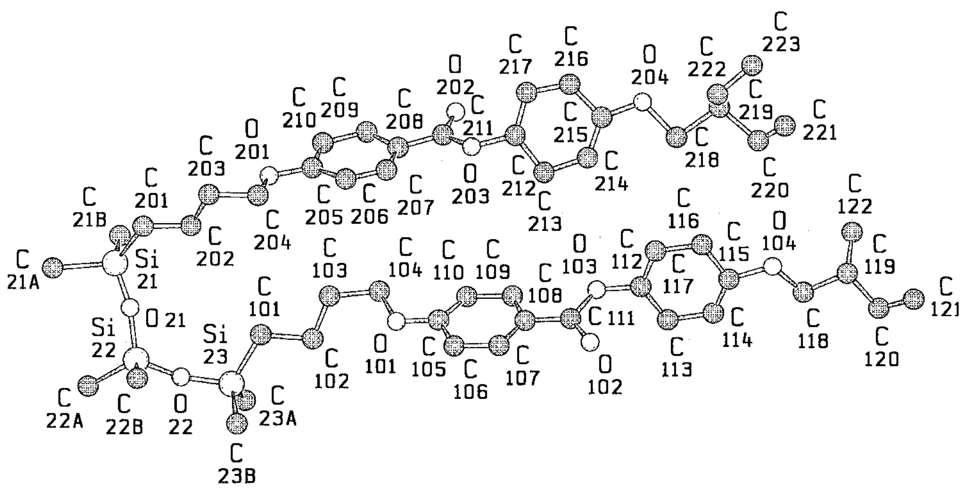


Figure 1. Representation of a single dimesogenic molecule of (−)4Dim showing a hairpin conformation and atom labelling.

Table 2. Fractional coordinates and isotropic displacement parameters B_{iso}, respective B_{eq} identified with *. Estimated standard deviations in parentheses. $B_{eq}=(4/3)\,[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

Atom	x	y	z	B/Å²
Si21	0.203(1)	−0.436(1)	−0.3817(6)	17.8(5)*
Si22	0.348(2)	−0.272(1)	−0.4519(5)	25.2(7)*
Si23	0.354(1)	0.0009(9)	−0.3996(5)	16.6(4)*
O21	0.289(2)	−0.349(2)	−0.4022(9)	20(1)*
O22	0.346(2)	−0.135(2)	−0.4353(9)	17.3(9)*
O101	0.397(1)	0.319(1)	−0.1612(6)	7.6(4)
O102	0.563(1)	0.808(1)	0.0271(7)	8.6(4)
O103	0.376(1)	0.783(1)	0.0443(6)	7.2(4)
O104	0.376(1)	1.190(1)	0.2249(7)	10.8(5)
O201	0.135(1)	−0.151(1)	−0.1540(6)	7.9(4)
O202	−0.096(1)	0.266(1)	0.0174(6)	8.3(4)
O203	0.099(1)	0.323(1)	0.0453(6)	7.8(4)
O204	0.033(1)	0.703(1)	0.2305(7)	9.6(5)
C21A	0.233(3)	−0.590(3)	−0.430(2)	19(1)*
C21B	0.040(4)	−0.424(5)	−0.396(2)	32(2)*
C22A	0.326(7)	−0.346(4)	−0.532(2)	39(3)*
C22B[a]	0.510	−0.272	−0.423	35.0
C23A	0.240(4)	0.074(3)	−0.447(2)	27(2)*
C23B	0.517(3)	0.048(3)	−0.400(2)	32(2)*
C101	0.330(2)	0.009(2)	−0.317(1)	10.0(8)
C102	0.325(2)	0.143(2)	−0.279(1)	8.3(7)
C103	0.296(2)	0.132(2)	−0.215(1)	7.6(6)
C104	0.272(2)	0.253(2)	−0.173(1)	8.4(7)
C105	0.397(2)	0.423(2)	−0.1224(9)	6.5(6)
C106	0.520(2)	0.477(2)	−0.1067(9)	5.9(6)
C107	0.547(2)	0.587(2)	−0.0593(8)	5.0(5)
C108	0.448(2)	0.633(2)	−0.0348(8)	4.8(5)
C109	0.332(2)	0.587(2)	−0.0481(8)	4.6(5)
C110	0.309(2)	0.478(2)	−0.0942(9)	6.6(6)
C111	0.462(2)	0.744(2)	0.010(1)	7.9(6)
C112	0.386(2)	0.888(2)	0.0894(9)	6.3(6)
C113	0.387(2)	0.999(2)	0.0686(9)	6.4(6)
C114	0.382(2)	1.103(2)	0.114(1)	7.9(6)
C115	0.379(2)	1.096(2)	0.172(1)	8.9(7)
C116	0.378(2)	0.985(2)	0.195(1)	8.1(7)
C117	0.382(2)	0.878(2)	0.149(1)	7.8(6)
C118	0.358(2)	1.306(2)	0.210(1)	11.4(8)
C119	0.357(3)	1.389(3)	0.274(2)	16(1)
C120	0.370(3)	1.515(3)	0.253(2)	18(1)
C121[b]	0.367(6)	1.582(6)	0.298(3)	21(3)
C122	0.240(3)	1.365(3)	0.298(2)	20(1)
C201	0.249(3)	−0.417(3)	−0.296(1)	14(1)
C202	0.226(2)	−0.296(2)	−0.259(1)	8.5(7)
C203	0.264(2)	−0.295(2)	−0.189(1)	9.0(7)
C204	0.263(2)	−0.173(2)	−0.149(1)	8.4(7)
C205	0.107(2)	−0.051(2)	−0.1151(9)	7.2(6)
C206	0.197(2)	0.033(2)	−0.0746(9)	6.7(6)
C207	0.165(2)	0.127(2)	−0.0376(9)	5.5(5)
C208	0.041(2)	0.148(2)	−0.0354(9)	5.4(5)
C209	−0.044(2)	0.061(2)	−0.0682(9)	6.4(6)
C210	−0.013(2)	−0.038(2)	−0.1111(9)	6.8(6)
C211	0.011(2)	0.251(2)	0.010(1)	8.5(7)
C212	0.079(2)	0.423(2)	0.090(1)	7.7(6)
C213	0.117(2)	0.534(2)	0.078(1)	7.9(6)
C214	0.101(2)	0.627(2)	0.129(1)	8.3(7)
C215	0.050(2)	0.619(2)	0.181(1)	8.0(6)

Table 2. (*continued*).

Atom	x	y	z	B/Å²
C216	0.012(2)	0.500(2)	0.186(1)	9.2(7)
C217	0.026(2)	0.400(2)	0.142(1)	7.1(6)
C218	0.076(2)	0.828(2)	0.225(1)	11.6(8)
C219	0.043(3)	0.900(3)	0.292(1)	15(1)
C220	0.072(4)	1.037(3)	0.289(2)	20(1)
C221[b]	0.09(1)	1.09(1)	0.345(6)	35(6)
C222	0.136(4)	0.863(4)	0.336(2)	22(2)
C223[b]	0.098(8)	0.912(7)	0.385(4)	30(4)

[a] Riding atom with fixed B_{iso} due to some strong correlations.
[b] Partial occupancy of approximately 0.5 assumed.

High mobility or disorder occur not only at the terminal groups, but also in the fold with high temperature factors for Si and the pendant methyl groups. The two Si–O–Si angles amount to *c.* 160° (table 3). The three atoms Si21, O21, and Si22 can be regarded as the head of the fold, and O22 as well as Si23 accommodate the branch 1 through C101, C102, etc. The length of the two branches 1 and 2 differ by *c.* 2.5 Å (C121..C22A: 25.7 Å, C221..C21A: 23.3 Å). The torsion angle leading to the first branch τ(C101–Si23–O22–Si22) is at −25° very small and contrasts with an expected *trans*- or *gauche*-conformation (table 4). The torsion angle leading to the second branch 2 of the hairpin τ(O21–Si21–C201–C202) amounts to 67° and represents a *gauche*-conformation.

Table 3. Selected bond lengths (Å) and bond angles (degrees) involving the fold in (−) 4Dim.

Bond lengths			Bond angles			
Si21	O21	1.52 (3)	O21	Si21	C201	105 (1)
Si21	C21A	1.94 (3)	O21	Si22	O22	116 (1)
Si21	C21B	1.84 (4)	O22	SI23	C101	110 (1)
Si21	C201	1.85 (3)	Si21	O21	Si22	157 (2)
Si22	O21	1.71 (3)	Si22	O22	Si23	164 (2)
Si22	O22	1.54 (2)	Si23	C101	C102	114 (2)
Si22	C22A	1.77 (4)	Si21	C201	C202	114 (2)
Si22	C22B	1.86 (2)	O21	Si21	C21A	103 (2)
Si23	O22	1.59 (2)	O21	Si21	C21B	120 (2)
Si23	C23A	1.88 (4)	C21A	Si21	C21B	106 (2)
Si23	C23B	1.89 (4)	C21A	Si21	C201	115 (2)
Si23	C101	1.86 (3)	C21B	Si21	C201	108 (2)
			O21	Si22	C22A	115 (2)
			O21	Si22	C22B	100 (1)
			O22	Si22	C22A	120 (2)
			O22	Si22	C22B	94 (1)
			C22A	Si22	C22B	107 (3)
			O22	Si23	C23A	105 (1)
			O22	Si23	C23B	102 (2)
			C23A	Si23	C23B	117 (2)
			C23A	Si23	C101	114 (2)
			C23B	Si23	C101	108 (1)

Table 4. Selected torsion angles τ concerning the fold in (−)4Dim (degrees).

Atom 1	Atom 2	Atom 3	Atom 4	Angle
O21	Si22	O22	Si23	41 (8)
O22	Si22	O21	Si21	118 (5)
C101	Si23	O22	Si22	−25 (7)
C201	Si21	O21	Si22	−175 (5)
O21	Si21	C201	C202	67 (2)
O22	Si23	C101	C102	−175 (2)
C105	O101	C104	C103	−176 (2)
C205	O201	C204	C203	172 (2)
Si23	C101	C102	C103	176 (2)
Si21	C201	C202	C203	178 (2)
C101	C102	C103	C104	−173 (2)
C201	C202	C203	C204	171 (2)
C102	C103	C104	O101	−68 (2)
C202	C203	C204	O201	68 (2)
C21A	Si21	O21	Si22	65 (5)
C21B	Si21	O21	Si22	−53 (5)
C21A	Si21	C201	C202	180 (2)
C21B	Si21	C201	C202	−62 (3)
C22A	Si22	O21	Si21	−28 (6)
C22B	Si22	O21	Si21	−143 (5)
C22A	Si22	O22	Si23	−175 (7)
C22B	Si22	O22	Si23	−62 (7)
C23A	Si23	O22	Si22	−148 (7)
C23B	Si23	O22	Si22	90 (7)
C23A	Si23	C101	C102	−57 (2)
C23B	Si23	C101	C102	75 (2)

The torsion angles involving the head group τ(O22−Si22−O21−Si21) = 118° and τ(O21−Si22−O22−Si23) = 41° cannot be described in common terminology. The alkoxy groups connected to the hairpin are in *all-trans*-positions except τ(C102−C103−C104−O101) = −68° and τ(C202−C203−C204−O201) = 68° both in *gauche*-conformations, but of opposite sign. Such *gauche*-positions are quite commonly observed for bridging oxygen leading to a benzene ring. The two least-squares planes describing the benzene rings are twisted for branch 1 by 79.8 (7)° and for branch 2 by 63.5 (7)°. It should be noted that the two molecules in the unit cell of *P*1 (or *P*-1) have opposite chirality (except the terminal groups) due to a pseudo-inversion centre which leads to an inversion of all torsion angles.

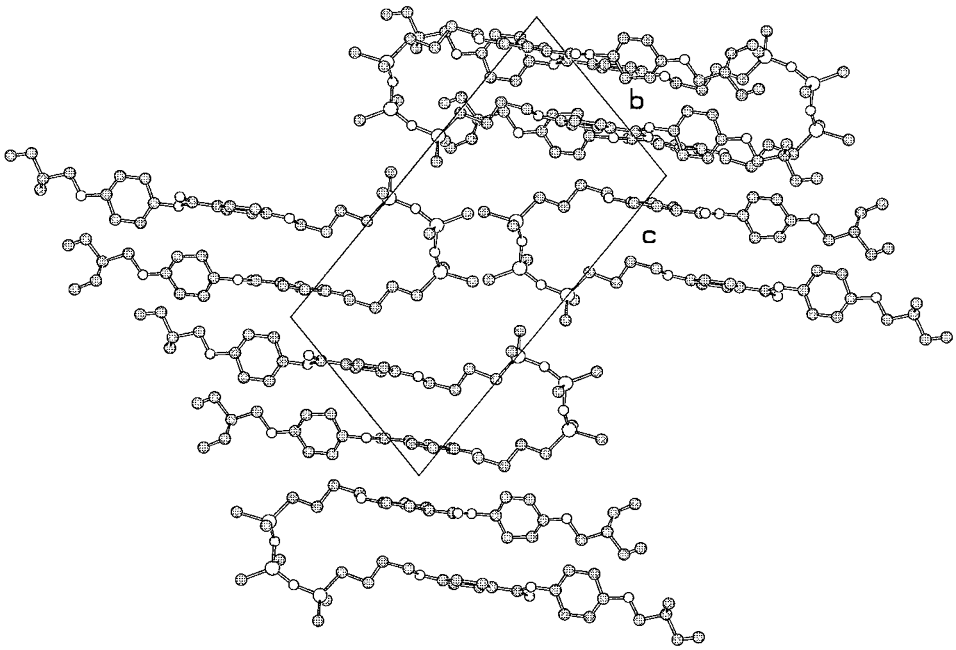
A hairpin conformation is quite unusual and may be caused here by the flexible siloxane groups. A sharply folded structure on a morphological scale was proposed for polymeric poly(tetramethyl-*p*-silphenylene siloxane) based on semi-empirical potential energy calculations with an adjacent re-entry fold which needed only a single monomeric residue [6]. In contrast, dimesogenic compounds connected by an alkylene spacer lead to extended molecular conformations in the crystalline and liquid crystalline state [7].

3.2. *Packing arrangement*

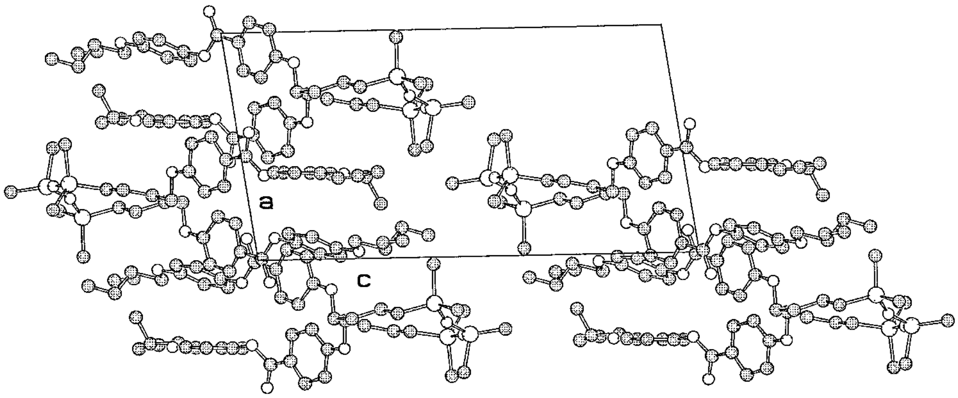
Figures 2 and 3 depict the arrangement of the molecules in the crystalline state. With a pseudo inversion centre at the origin of the unit cell, it is apparent in figure 2 (*a*) that the hairpins (folds) appear at opposite ends of adjacent sheets at van der Waals distances and provide the impression of a closed structure in [1 0 0] projection. The hexamethyltrisiloxane groups of adjacent molecules are not in fact facing each other as suggested in figure 2 (*a*) in [1 0 0] projection; rather they are shifted in the [1 0 0] direction as demonstrated in figure 2 (*b*). Listed in table 5 are the closest contacts between Si and Si, as well as between Si and the pendant methyl groups; these primarily involve Si23 and Si22 represented in the centre of the projected unit cell in figure 2 (*b*) and along the *c*-line of the unit cell in figure 2 (*a*). Strings of molecules in head to tail fashion, pointing in one direction, can be defined as shown in figures 2 (*b*) and 3. A complete overlap of molecules is observed when projected down

Table 5. Short packing contacts below a given limit. Symmetry operation applied to the second atom.

Atoms		Distance/ Å	Symmetry
Si23	Si23	5.82	$(-x+1, -y, -z-1)$
< 5.50 Å			
Si22	O104	5.42	$(-x+1, -y+1, -z)$
Si23	O104	5.45	$(-x+1, -y+1, -z)$
SI23	O22	5.62	$(-x+1, -y, -z-1)$
< 5.20 Å			
Si23	C23B	4.75	$(-x+1, -y, -z-1)$
Si22	C23B	4.85	$(-x+1, -y, -z-1)$
Si23	C116	5.06	$(-x+1, -y+1, -z)$
Si23	C21A	5.08	$(x, y+1, z)$
Si23	C223	5.13	$(x, y-1, z-1)$
Si22	C223	5.13	$(x, y-1, z-1)$
Si21	C119	5.17	$(-x+1, -y+1, -z)$
SI21	C21B	5.21	$(x, y-1, z-1)$
< 3.60 Å			
C107	C108	3.56	$(-x+1, -y+1, -z)$
C107	C109	3.56	$(-x+1, -y+1, -z)$
C106	C108	3.56	$(-x+1, -y+1, -z)$
C106	C111	3.59	$(-x+1, -y+1, -z)$
C209	C209	3.59	$(-x, -y, -z)$
C208	C209	3.60	$(-x, -y, -z)$
C210	C211	3.60	$(-x, -y, -z)$
< 3.50 Å			
O103	O202	3.25	$(-x, -y+1, -z)$
< 3.50 Å			
C207	O102	3.10	$(-x+1, -y+1, -z)$
C206	O102	3.13	$(-x+1, -y+1, -z)$
C109	O202	3.28	$(-x, -y+1, -z)$
C217	O201	3.38	$(-x, -y, -z)$
C213	O202	3.38	$(-x, -y+1, -z)$
C113	O102	3.40	$(-x+1, -y+2, -z)$
C117	O101	3.46	$(-x+1, -y+1, -z)$



(*a*)



(*b*)

Figure 2. Representation of the packing arrangement for (−)4Dim: (*a*) in the [1 0 0] direction and (*b*) in the [0 1 0] direction. A reversal of the head to tail direction of the neighbouring molecules is present, shifted in the *a*-direction as demonstrated for the top two molecules in (*a*).

the string axis (figure 3). All strings lying in a single plane parallel to b–c point with their heads in the same direction, those strings in the two adjacent planes pointing in the opposite direction. Considering now the interaction with the neighbouring sheet below or above, the siloxane units are facing the terminal groups of the dimesogenic compound and the argument concerning separation of siloxane groups in layers causing the folds does not hold [8]. The shortest contacts excluding hydrogen are listed in table 5 and have the expected values. They primarily occur in the planes running diagonally or along a in figure 3. The pseudo inversion centre at the origin causes an inversion of the molecules placed in respective strings lying in the diagonal planes (figure 3).

The longest d-spacing (0 0 1) amounts to 21.32 Å for (−)4Dim. This distance lies within the experimental error of the published layer spacing of the small angle X-ray reflection of 21.57 Å [1] and corresponds to half the length of the extended molecule.

4. Conclusions

A hairpin conformation has been established for the dimesogenic compound (−)4Dim in which the two mesogenic moieties are connected by a hexamethyltrisiloxane group. Although this compound exhibits only crystalline states, the result concerning a hairpin conformation can be extended to other crystalline and liquid crystalline states of the homologous series with

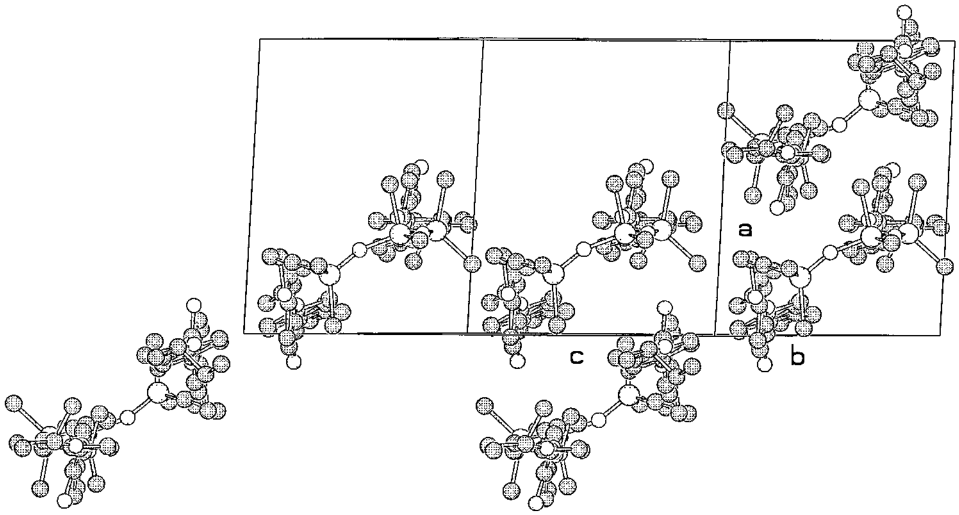


Figure 3. Representation of the packing arrangement down the hairpin axis for (−)4Dim.

$m = 3$–11 (*cf.* the scheme) reported elsewhere, since the X-ray patterns for the crystals and the liquid crystals show the same features in the small angle region; that is, approximately half the *d*-spacing expected for the extended length of the molecules [1, 2]. However, the packing arrangement may differ for other members of the homologous series as can already be concluded from the size of the unit cell of another crystalline compound of this series which contains 4 molecules [1] in the unit cell instead of the 2 as reported here for (−)4Dim.

It is well known that the siloxane unit connected to longer chains or as a spacer represents a flexible moiety leading, for example, to polysiloxane rings of small sizes. This flexibility is confirmed by the present investigation and only two units are necessary for (−)4Dim to form a sharp hairpin.

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References

[1] Kaeding, A., and Zugenmaier, P., 1998, *Liq. Cryst.*, **25,** 449.

[2] Kaeding, A., 1998, Dissertation, TU Clausthal, D-38678 Clausthal-Zellerfeld, Germany.

[3] *MolEN, 1990*, an interactive structure solution procedure, Enraf-Nonius, Delft, The Netherlands.

[4] Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Burla, M. C., Polidori, G., Camalli, M., and Spagna, R., 1997, *SIR97*, a package for crystal structure solution by direct methods and refinement.

[5] Keller, E., 1992, *SCHAKAL 92*, a computer program for the graphic representation of molecular and crystallographic models, Kristallographisches Institut der Universität Freiburg i. Br., Germany.

[6] Gardner, K. H., Magill, J. H., and Atkins, E. D. T., 1978, *Polymer*, **19,** 370.

[7] Heinemann, F., and Zugenmaier, P., 2000, *Mol. Cryst. liq. Cryst.*, **348,** 239 and 255.

[8] Corsellis, F., Guillon, D., Kloess, P., and Coles, H., 1997, *Liq. Cryst.*, **23,** 235.