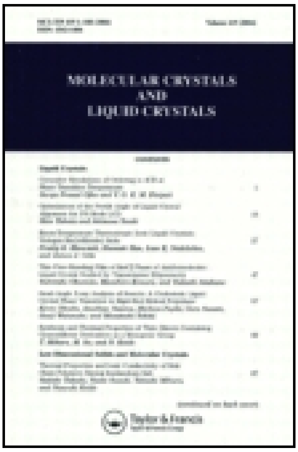

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Crystal and Molecular Structure of 3,3′-Sulphur-bis [methyl 4-(4-methyl-benzoyloxy)-benzoate as a Model Compound of Sulphur Ligated Siamese Twin Mesogens

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Crystal and Molecular Structure of 3,3′-Sulphur-bis [methyl 4-(4-methylbenzoyloxy)-benzoate] as a Model Compound of Sulphur Ligated Siamese Twin Mesogens

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In order to enlighten the molecular structure of sulphur ligated siamese twin mesogens we were interested in X-ray crystal structure determinations of such substances. Single crystals suitable for X-ray investigations couldn't be obtained of the mesogenic sulphinyl and sulphonyl ligated twins but of the non-mesogenic sulphide $(CH_3—C_6H_4—CO(O)—C_6H_3—CO(O)—CH_3)_2S$ $\underline{2}$ which can be used as a model for the just-mentioned mesogens.

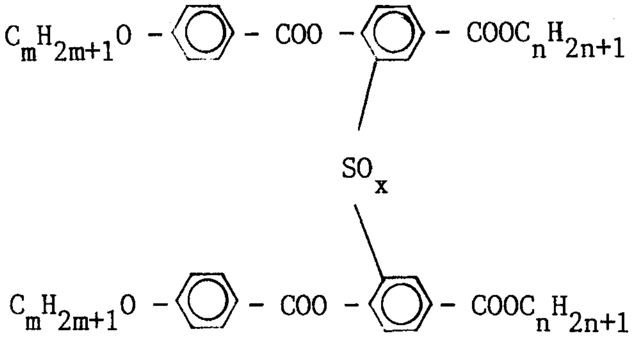
The title compound $\underline{2}$ crystallizes in the monoclinic space group C2/c with a = 10.703(2), b = 9.374(1), c = 29.206(5), Å, β = 111.49(1)° and four molecules per unit cell. The structure was solved by direct methods and refined to R = 0.044. The molecules have exact C_2 symmetry and a gabled roof-like shape. The two halves of one twin molecule adopt each a fully stretched and nearly linear conformation and are antiparallel oriented to each other.

Keywords: Sulphur ligated twins, siamese twin mesogens, molecular structure, crystal structure, X-ray analysis

INTRODUCTION

For about 15 years, the attempts to exceed the borders of Vorländer's rod-like molecular model of thermotropic liquid crystals have led to interesting new mesogenic compounds, among those the "discotics" are the most important examples for new structural types. A review on contemporarily new structures is given by Demus.[1]

In this context we have been interested for a few years in ligated siamese twin mesogens in which two mesogenic halves of a molecule are linked laterally by a ligating group. We reported about ligated twins with 4,4′-disubstituted phenyl benzoates as molecular halves and —S—, —SO— or —SO$_2$— as the ligating group[2]:



1a

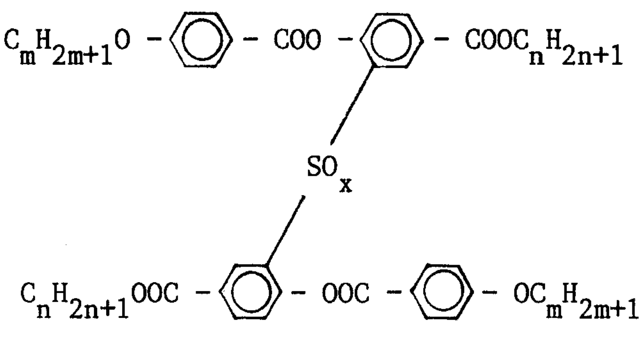
x = 0, 1, 2

m = 1, 2, ..., 10

n = 1, 2, 3, 4

The sulphur ligated twins (1; $x = 0$) are not mesogenic, but the sulphinyl (1; $x = 1$) and sulphonyl (1; $x = 2$) ligated twins form nematic phases which can be transformed into nematic glasses with glass transition temperatures above room temperature.[3]

For all compounds 1 there are to be discussed mainly the two conformations 1a and 1b resulting from a rotation around the C—S bond and leading to a stretched molecular shape (according to the Vorländer model).

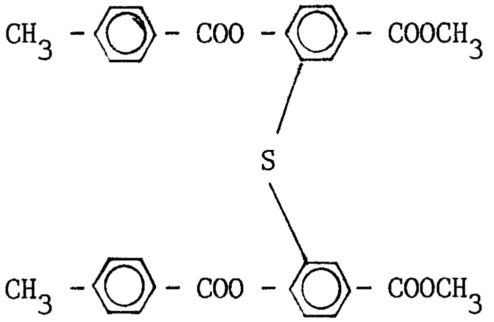


1b

In conformation 1a both halves of the molecule are ordered parallel, but in conformation 1b antiparallel. Especially for higher numbers of *m* and lower numbers of *n* (particularly for $n = 1$), the length-to-width ratio (decisive for the mesogenic power of compounds according to the rod-like molecular model) is greater in conformation 1b than in 1a.

From the thermal behavior, from the comparison between dielectric anisotropies of non-ligated phenyl benzoates and those of analogous sulphonyl ligated compounds and from the results of X-ray diffraction measurements performed on oriented nematic samples we concluded that twin compounds are most likely to exist in the nematic phase in the antiparallel conformation 1b.[3]

In contrast to many previous unsuccessful attempts to prepare suitable single crystals of mesogenic sulphur ligated twins, recently we succeeded in the case of the very simple twin 3,3′-sulphur-bis [methyl 4-(4-methyl-benzoyloxy)-benzoate]:



2

This compound is not a mesogen but can be used as a suitable model of long-chain substituted mesogenic sulphinyl and sulphonyl ligated twins.

CRYSTAL AND MOLECULAR STRUCTURE

The molecular structure of 2 including atomic numbering is illustrated in Figures 1 and 2, bond lengths and angles are given in Tables I and II.

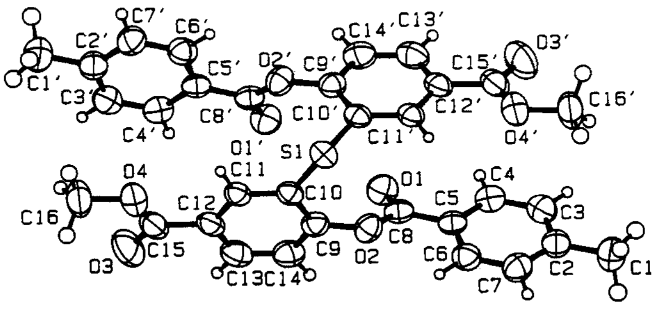


FIGURE 1 Molecular structure of 2 with the atom labelling used in the X-ray analysis.

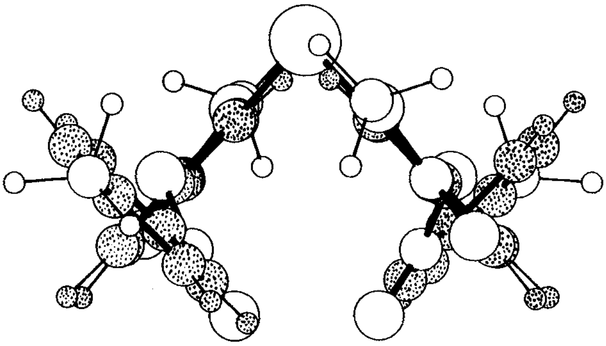


FIGURE 2 Molecular structure of 2 viewed perpendicular to the twofold axis and approximately parallel to the molecular long axis (benzene ring atoms are dotted).

TABLE I

Bond lengths for non-H atoms (Å)

C1 - C2	1.509(4)	C2 - C3	1.390(5)
C2 - C7	1.395(5)	C3 - C4	1.386(4)
C4 - C5	1.387(4)	C5 - C6	1.387(4)
C5 - C8	1.472(3)	C6 - C7	1.378(4)
C8 - O1	1.197(4)	C8 - O2	1.373(3)
C9 - C10	1.390(4)	C9 - C14	1.377(5)
C9 - O2	1.388(3)	C10 - C11	1.386(3)
C10 - S1	1.784(3)	C11 - C12	1.383(4)
C12 - C13	1.393(5)	C12 - C15	1.485(4)
C13 - C14	1.386(4)	C15 - O3	1.213(4)
C15 - O4	1.329(4)	C16 - O4	1.451(3)

TABLE II

Bond angles for non-H atoms (°)

C1 - C2 - C7	120.6(3)	C1 - C2 - C3	121.6(3)
C3 - C2 - C7	117.9(3)	C2 - C3 - C4	121.2(3)
C3 - C4 - C5	120.2(3)	C4 - C5 - C8	119.0(3)
C4 - C5 - C6	119.1(3)	C6 - C5 - C8	122.0(3)
C5 - C6 - C7	120.5(3)	C2 - C7 - C6	121.1(3)
C5 - C8 - O2	110.4(3)	C5 - C8 - O1	127.0(3)
O1 - C8 - O2	122.6(3)	C14 - C9 - O2	120.0(3)
C10 - C9 - O2	118.6(3)	C10 - C9 - C14	121.1(3)
C9 - C10 - S1	121.6(2)	C9 - C10 - C11	119.0(3)
C11 - C10 - S1	119.3(2)	C10 - C11 - C12	120.7(2)
C11 - C12 - C15	121.6(3)	C11 - C12 - C13	119.4(3)
C13 - C12 - C15	119.0(3)	C12 - C13 - C14	120.4(3)
C9 - C14 - C13	119.3(3)	C12 - C15 - O4	112.8(3)
C12 - C15 - O3	124.1(3)	O3 - C15 - O4	123.1(3)
C8 - O2 - C9	120.0(2)	C15 - O4 - C16	116.5(3)
C10 - S1 - C10'	100.4(1)		

As pointed out in the introduction, of particular interest in the structure of 2 is the orientation of the two halves of the ligated twin molecule. The antiparallel orientation of the two substituted phenyl benzoate moieties suggested by dielectric and X-ray investigations for the nematic phase, is perfectly realized in the crystalline state of 2. Required by the space group symmetry, the molecule exhibits exact C_2 symmetry with the bridging sulphur atom located on the crystallographic twofold axis. The methyl 4-(4-methyl-benzoyloxy)-benzoate fragments have an optimum stretched and nearly linear shape. This is based on the stereochemistry of the carboxylic groups as planar bridging structural components with parallel configuration introducing only a parallel displacement of the moieties they connect. Thus, the torsion angles C5-C8-02-C9 and C12-C15-04-C16 amount to $-175.8(2)$ and 179.3(3)°, respectively. The phenyl rings I (C2. . .C7) and II (C9. . .C14) as well as the carboxylic groups III (C5,C8,01,02) and IV (C12,C15,03,04) are planar within experimental error and make the following interplanar angles: I/II 86.4, I/III 15.6, II/III 71.6, II/IV 6.6°. These values agree well with the results of previous investigations on phenyl benzoates.[4] Caused by the value of 100.4(1)° for the bond angle C10-S1-C10′, the molecule has a gabled roof-like shape illustrated by Figure 2. The interplanar angles between the phenyl rings and carboxylic groups (defined as before) of the two symmetry-equivalent molecular halves are I/I′ 2.8, I/IV′ 8.5, II/II′ 85.2, II/III′ 15.4°.

All bond lengths and angles in 2 (cf. Tables I and II) are in good agreement with standard values and require no comment. The observed and refined C—H bond lengths range from 0.97(3) to 1.02(3)° with a mean of 0.99(2)°.

The crystal packing of the molecules is illustrated in Figure 3. The molecules

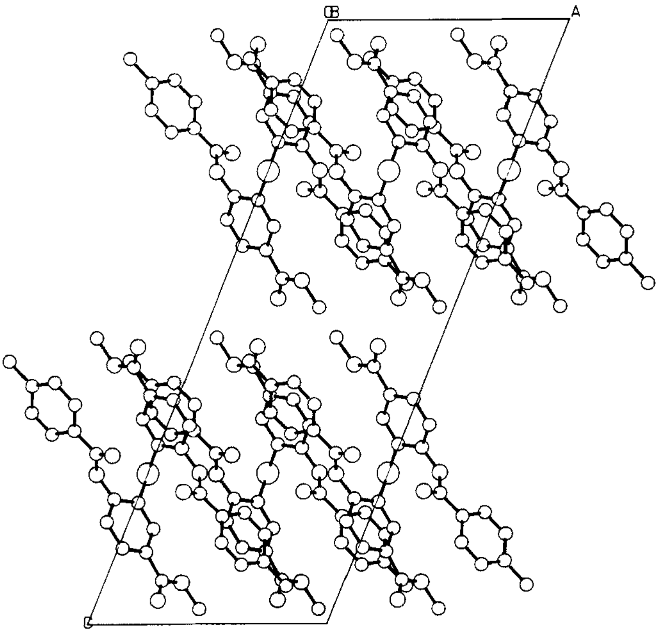


FIGURE 3 Crystal structure of 2 projected along [010].

are arranged in the unit cell in two smectic-like layers, one layer containing molecules with their sulphur atom in $z/c = \frac{1}{4}$ and the other one with S in $z/c = \frac{3}{4}$. The layer planes are parallel to (001) and the molecular long axes, defined as the lines connecting the centres of the two phenyl rings in each twin half, are inclined to the layer normal by a tilt angle of 33.5°. The structural principle of antiparallelism found for the two wings of one molecule is passed on to the packing scheme: Neighbouring twin halves of different molecules within one layer are also packed in a head-to-tail fashion.

Judging from non-H intermolecular atomic distances there is no indication of other than normal van der Waals forces within the crystal lattice.

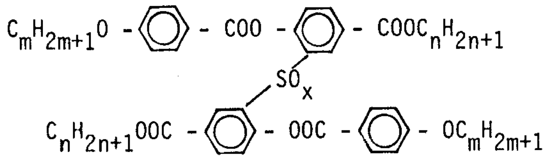
Discussion of the Molecular Structure of S-ligated Twin Mesogens in the Liquid-crystalline Phase

The antiparallel orientation of the molecular halves of compound 2 proved for the crystalline state should be additionally fixed by the bridging sulphinyl or sulphonyl group replacing the sulphur atom due to the lone pair electrons of the oxygen atom(s).

A comparison between selected analogous sulphides, sulphoxides and sulphones shows a distinct increase of liquid-crystallinity in the series from —S— to —SO— to —SO_2— as ligating group between the two molecular halves[3] (cf. Table III). In our opinion, for an explanation of this tendency not only the increasing polarizability of the ligating group in the above-mentioned order but also the influence of the molecular geometry must be considered. During melting the mutual mobility of the two twin halves considerably increases. Therefore, we assume that in the

TABLE III

Mesogenic behaviour of selected analogous twin compounds



Type of compound	x	m	n	T_m/°C	T_{NI}/°C
Sulphide	0	6	1	138	-
Sulphoxide	1	6	1	146	(121)
Sulphone	2	6	1	152	163
Sulphide	0	8	1	142	-
Sulphoxide	1	8	1	131	(119)
Sulphone	2	8	1	139	151

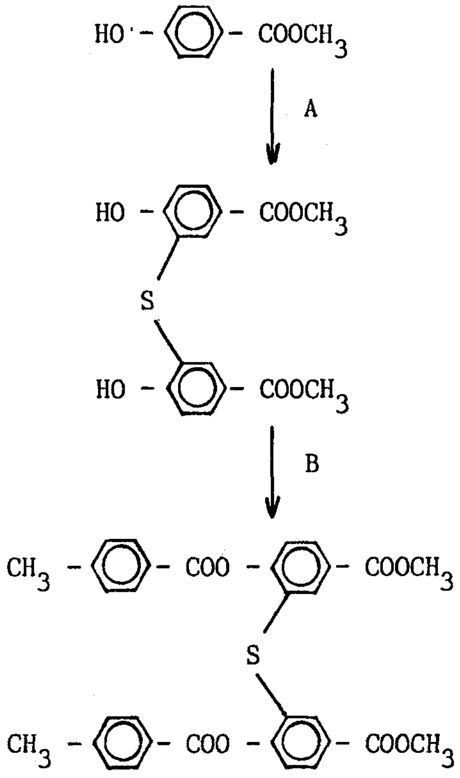
sulphides the strong antiparallel orientation of the molecular halves is lost and, as a result of the multitude of possible conformations, the stretched linear molecular shape is probably not realized for the majority of the molecules. In contrast to the sulphide, in the sulphoxide and even more in the sulphone molecule, the oxygen in the ligating group is expected to stabilize the roof-like arrangement of the benzene rings and so to support the maintenance of the antiparallel conformation 1b during melting. Our assumption is supported by the appearance of mesophases for these compounds and the non-appearance for the sulphides.

The observed molecular structure of compound 2 is in agreement with the results of dielectric and X-ray investigations in the nematic phase of analogous sulphonyl ligated twins[3] (cf. the introduction to this paper). Therefore, although the investigated compound 2 as the simplest S-ligated twin is a non-mesogen, the results of its structure analysis can be considered rather certainly to be a useful model of the molecular shape of the analogous liquid crystalline siamese twins 1.

EXPERIMENTAL

Synthesis

Compound 2 was obtained in a good yield by using the following simple procedure:



The sulphurization (A) was carried out applying the method of Denisova *et al.*[5]:

3,3′-Sulphur-bis(methyl 4-hydroxy-benzoate). 60.4 g (0.4 mol) methyl 4-hydroxy-benzoate were suspended with 2.6 g (0.02 mol) $ZnCl_2$ in 180 ml dry dichloromethane and stirred for 20 min at room temperature. A solution of 16.2 ml (0.2 mol) disulphurdichloride in 20 ml dry dichloromethane was dropped into the refluxing mixture for two hours. The beginning of the reaction was indicated by a rapid generation of HCl gas and a gradual solution of the suspended ester. After three more hours the precipitated sulphide was filtered off, boiled for some minutes in 150 ml water and dried. The crude product was recrystallized from 50% acetic acid. m.p. 184–186°C, 80% yield.

The acylation (B) was performed using the Einhorn method[6]:

3,3′-Sulphur-bis [methyl 4-(4-methyl-benzoyloxy)-benzoate]. 1 g (3 mmol) 3,3′-sulphur-bis (methyl 4-hydroxy-benzoate) was solved in 10 ml pyridine and 0.97 g (6 mmol) 4-methyl-benzoyl chloride were added dropwise. The mixture was refluxed for 30 min in a water bath and then poured into an ice/HCl mixture, filtered, dried and recrystallized from toluene. m.p. 187°C, 70% yield.

Crystal Structure Determination

Optically clear colorless crystals of 2 were grown from toluene. Preliminary investigations by film methods revealed a monoclinic unit cell and space group C2/c. A crystal with approximate dimensions 0.4 × 0.3 × 0.3 mm was mounted on a Syntex $P2_1$ diffractometer to determine exact lattice parameters by a least squares treatment of the setting angles for 15 reflections as well as to collect intensity data, both using graphite monochromatized CuKα radiation. Relevant crystal data are summarized in Table IV. 1844 unique intensity data were measured in $\Theta/2\Theta$ scan (bisecting mode) for $2\Theta \leq 115°$ and h, k, l from $\bar{1}\bar{1}$, 0, 0 to 11, 10, 31. The intensities

TABLE IV

Crystal data

Table IV Crystal Data

$C_{32}H_{26}O_8S$
$M = 570.62$ g mol^{-1}
monoclinic, space group C2/c

$a = 10.703(2)$ Å	$Z = 4$
$b = 9.374(1)$ Å	$D_m = 1.39$ g cm^{-3}
$c = 29.206(5)$ Å	$D_x = 1.390$ g cm^{-3}
$\beta = 111.49(1)°$	$F(000) = 1192$
$V = 2726.5(8)$ Å^3	$\mu(CuK\alpha) = 14.6$ cm^{-1}

TABLE V

Final positional and equivalent isotropic displacement parameters for non-H atoms
$U_{eq} = (\frac{1}{3})\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
C1	1.2655(3)	0.3577(4)	0.93665(13)	0.0809(15)
C2	1.1319(3)	0.3874(3)	0.89634(11)	0.0599(13)
C3	1.0443(3)	0.4894(3)	0.90190(11)	0.0615(12)
C4	0.9213(3)	0.5154(3)	0.86485(11)	0.0572(13)
C5	0.8823(3)	0.4375(3)	0.82148(10)	0.0479(11)
C6	0.9687(3)	0.3352(3)	0.81558(11)	0.0580(14)
C7	1.0922(3)	0.3119(3)	0.85213(12)	0.0646(14)
C8	0.7509(3)	0.4674(3)	0.78278(10)	0.0512(11)
C9	0.5983(3)	0.3692(3)	0.70756(10)	0.0512(11)
C10	0.4939(3)	0.2746(3)	0.70232(9)	0.0458(11)
C11	0.3848(3)	0.2717(3)	0.65825(9)	0.0484(10)
C12	0.3780(3)	0.3635(3)	0.62035(10)	0.0536(12)
C13	0.4815(3)	0.4608(4)	0.62696(12)	0.0669(15)
C14	0.5921(3)	0.4633(3)	0.67058(12)	0.0661(15)
C15	0.2625(3)	0.3616(4)	0.57269(11)	0.0656(14)
C16	0.0610(4)	0.2459(5)	0.52429(12)	0.0895(17)
O1	0.6803(2)	0.5685(2)	0.78017(7)	0.0655(9)
O2	0.7148(2)	0.3585(2)	0.74902(7)	0.0586(8)
O3	0.2466(3)	0.4470(3)	0.53984(8)	0.1005(12)
O4	0.1778(2)	0.2551(2)	0.56951(7)	0.0737(9)
S1	0.5	0.15274(10)	0.75	0.0512(4)

of two check reflections varied by ±1.5% for 006 and ±1.7% for 202. 1674 reflections had intensities $I \geq 1.96\sigma(I)$ and were considered observed. Lp corrections were applied during data reduction while absorption effects were neglected.

The structure was solved by the direct methods option of SHELXS-86.[7] The resulting E-map showed all 21 non-hydrogen atomic positions with $R = 0.187$. Subsequent refinement of these positions with at first isotropic and then anisotropic displacement parameters in several full-matrix least-squares cycles on F^2 reduced R to 0.096. The positions of the H atoms at the phenyl rings found in a difference Fourier map were refined with isotropic displacement parameters, the methyl groups were treated as rigid rotating groups, giving a final R value of 0.044 ($R_w = 0.047$). Weights $w = 1/\sigma^2(F_o)$ were applied during the last cycles of refinement along with an empirical extinction correction on F_c ($F_{corr} = F_c(1 - \chi.10^{-4}F_c^2/\sin\Theta)$, χ refining to 0.0048(2)). 8.12 reflections per parameter were available, the maximum shift/σ during the last refinement cycle was 0.274, the final difference Fourier map showed maximum and minimum electron density of 0.215 and -0.236 eA^{-3}, respectively.

All calculations were done on IBM compatible PC's using the program packages SHELXS-86,[7] SHELX-76[8] and EDIT.[9]

Positional and equivalent isotropic displacement parameters for non-hydrogen atoms are listed in Table V.

Acknowledgment

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