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J. Them [a] , V. Vill [b] & F. Fischer [c]

[a] Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, Orleans-Ring 23, D-4400, Münster, Fed. Rep. Germany

[b] Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, Orléans-Ring 23, and Physikalisches Institut, Westfälische Wilhelms-Universität, Wilhelm-Klemm-Str. 10, D-4400, Münster, Fed. Rep. Germany

[c] Physikalisches Institut, Westfälische Wilhelms-Universität, Wilhelm-Klemm-Str. 10, D-4400, Münster, Fed. Rep. Germany

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Synthesis, Properties and Conformations of Liquid Crystalline 1,4-Dioxanes and Comparison with the Corresponding 1,4-Dithiane, Cyclohexane, and Benzene Derivatives

J. THIEM

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, Orléans-Ring 23, D-4400 Münster, Fed. Rep. Germany

and

V. VILL

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, Orléans-Ring 23, and Physikalisches Institut, Westfälische Wilhelms-Universität, Wilhelm-Klemm-Str. 10, D-4400 Münster, Fed. Rep. Germany

and

F. FISCHER

Physikalisches Institut, Westfälische Wilhelms-Universität, Wilhelm-Klemm-Str. 10, D-4400 Münster, Fed. Rep. Germany

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The preparation and mesomorphic properties of a series of *bis*-(4-alkyl- or 4-alkoxy-benzoyloxy)-*trans*-1,4-dioxanes 1, *trans*-1,4-dithianes 2 and *trans*-1,4-cyclohexanes 3 are reported and compared to the corresponding hydroquinone *bis*-esters 4. The 1,4-dithianes 2 do not show liquid crystalline properties and the 1,4-dioxanes 1 in their *trans* diaxial conformation are less favorable for nematic phases than the corresponding cyclohexanes 3 which are predominantly in the diequatorial conformation. However, owing to the cross-dipole moments they seem to be of advantage in stabilizing smectic phases.

Keywords: liquid crystalline heterocycles, 1,4-dioxane, 1,4-dithiane, conformation, anomeric effect

INTRODUCTION

As part of a program aimed at studying heterocyclic liquid crystalline compounds we were interested in a systematic survey of 1,4-dioxane derivatives. Previously a

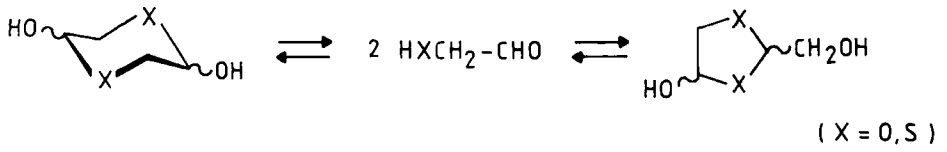


FIGURE 1 Dissociation equilibrium of *trans*-2,5-dihydroxy-1,4-dioxane (1,4-dithiane).

number of liquid crystalline 1,3-dioxanes had been prepared and their properties studied;[1] these were generally similar to those of the analogous cyclohexanes. However, the former show enhanced clearing temperatures which represent a favorable property. Therefore it was of particular interest to investigate whether such advantageous properties due to the influence of the ring oxygen would be general. Thus the present study is devoted to the group of 1,4-dioxanes.

RESULTS AND DISCUSSION

For the preparation of the *bis*-(*p*-alkylbenzoates) as well as the *bis*-(*p*-alkoxybenzoates) of *trans*-2,5-dihydroxy-1,4-dioxane (1-series), *trans*-2,5-dihydroxy-1,4-dithiane (2-series), and *trans*-cyclohexane-1,4-diol (3-series), general esterification procedures were followed. The resulting material was usually purified by column chromatography and recrystallized.

For glycol aldehyde (X = O), the solid state is represented by *trans*-2,5-dihydroxy-1,4-dioxane.[2] In solution, however, an equilibrium between the monomeric state and the various six- and five-membered dimeric forms occurs (Figure 1). During the esterification significantly lower yields are obtained in comparison to those with the corresponding cyclohexane. Although the solid dimer was employed to give the *trans*-2,5-diacyl derivatives, a certain amount of isomerization may occur in the course of the reaction, and lead to a series of side product esters which must be separated by chromatography.

Configuration and conformation of the derivatives have been unequivocally assigned by ^{1}H NMR spectroscopy. As expected, for the ring protons H–2, H–3a, and H–3e, double intensities are observed. The equatorial position of H–2 in all compounds of the 1-series becomes evident by the small coupling constants $J_{2,3a} < 0.5$ and $J_{2,3e} \approx 1.5$ Hz which substantiate the axial-equatorial, or di-axial arrangement, respectively. Thus, in solution, in all these compounds, the ester groups adopt predominantly the axial position which is fully in accord with a double operation of a large anomeric effect for benzoates (Figure 2).[3,4]

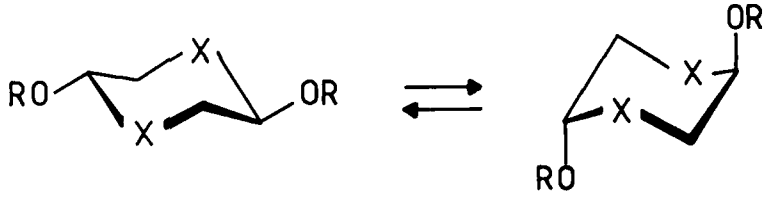


FIGURE 2 Conformational equilibria of *trans*-1,4-disubstituted cyclohexanes (X = CH_2) and 2,5-disubstituted-1,4-dioxanes (X = O) or dithianes (X = S).

In one case the glycol aldehyde, dissolved in anhydrous pyridine, was treated with 4-hexyloxybenzoyl chloride, and this led to a number of compounds. By a series of fractional crystallizations and column separations the overall yield decreased. However, in addition to the desired *trans*-diester 1g (13%), the acylated glycol aldehyde (11%), the mono-acylated six-membered ring dimer (4%), and the 1,4-*cis* diester (2%) were obtained.[5]

The 4-alkylbenzoates 1a and 1b did not show liquid crystalline phases, and with the 4-alkoxybenzoates only monotropic phases were observed (Table I). For 1e, 1f, and 1g, nematic phases were unequivocally detected by the schlieren texture in thick, and the marbled texture in thin layers. In addition, 1e exhibits a smectic A phase as is evident by a simple fan texture. Other derivatives of the 1 and 3 series could not be supercooled far enough to enable the observation of a S_A phase. The diester 1h which crystallizes at 80°C does not show any mesophase on supercooling below that point but in 1i a phase with a higher clearing point of 85°C is observed. This phase occurred as a Schlieren texture and is tentatively assigned as a smectic C phase. S_A phases do not, but S_C phases may, show schlieren textures.[6] Further, an S_B or other higher-ordered smectic phases may be ruled out because of the low viscosity. Finally, the phase seems unlikely to be nematic because never before has such an increase in the clearing points in a homologous series been observed.[7]

The dimer of thioglycol aldehyde,[8] *trans*-2,5-dihydroxyl-1,4-dithiane (X = S) represents a double hemimercaptal which is considerably more stable than the oxygen analog. Consequently in the esterification reaction much better yields were obtained. Again, in solution, both the ester functions adopt axial arrangements as evidenced by the small coupling constants of 2b, 2d, 2e, and 2g ($J_{2,3a} \approx 4.5$ and $J_{2,3e} \approx 1.4$ Hz) and this is expected, again because of the anomeric effect. None of these derivatives show any liquid crystalline phases even when supercooled, e.g., 2e was cooled at 110°C (Table I).

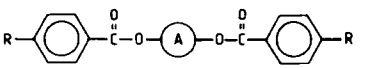
By fractional crystallization of *cis/trans*-1,4-diacetoxycyclohexane the *trans* derivative was obtained[9] and used for peresterifications to give the 3-series compounds in generally high yields. There is ample evidence that in solution cyclohexanes prefer chair conformations and sterically demanding substituents adopt equatorial arrangements.[10,11] Consequently *trans*-1,4-di-substituted derivatives should prefer the diequatorial conformation, and a similar finding in the solid state was proven by x-ray studies for *trans*-1,4-dibenzoyloxy cyclohexane.[12] However, in solvents with increasing polarity, two polar 1,4-substitutents increasingly will prefer the diaxial positions. Thus for the *trans*-1,4-diacyloxy cyclohexane (acetyl to trichloroacetyl residues), the amount of diaxial conformer rose from 42.7 to 89.3%.[13] This may be correlated to the width of the H-1 and H-4 signals in the ^{1}H NMR spectra which in the former case is larger and in the latter smaller, owing to the sum of the vicinal coupling constants.

In the present cases the compounds 3 show signals of smaller width, but the slow ring inversion prohibits observation of resolved signals. Nevertheless, these findings point to prevailing diaxial arrangements of the ester groups.

The nematic phases in 3a, 3b, 3d,[14] 3e and 3h (Table I) were unequivocally assigned by their schlieren or marbled textures as described above. For compound

TABLE I

Transition temperatures for compounds of structure



R	A	1			2			3[a]			4[a]			
a	H_3C	K 204.5		I			K 173.5	(N 137)	I	K 236		(N 231.5)	I^{21}
b	$H_{11}C_5$	K 99		I	K 123	I	K 136	(N 102)	I	K 125		N 188	I^{18}
c	$H_{17}C_8$						K 118.5		I	K 115		N 156	I^{18}
d	H_3CO	K 206		I	K 200	I	K 199.5	(N 197.5)	I[b]	K 217	S 178	N 301	I^{15}
e	H_5C_2O	K 193 (S_A 103 N 119)		I	K 209	I	K 178.5	N 200.5	I	K 226		N 287	I^{22}
f	H_9C_4O	K 155	(N 97)	I			K 129	N 157	I^{24}	K 153		N 241	I^{22}
g	$H_{13}C_6O$	K 112	(N 83)	I	K 129	I	K 122	N 136	I^{24}	K 124.4		N 212.9	I^{17}
h	$H_{25}C_{12}O$	K 114		I			K 112	N 113	I	K 109.1	S 115.7	N 171.5	I^{17}
i	$H_{33}C_{16}O$	K 117 (S_C 85)		I			K 108 (S_C 106)		I	K 108.1	S 156.4		I^{17}

[a] Data for some cyclohexane (3) and the benzene derivatives 4 are taken from the literature (cf. reference number);
[b] lit. [14]: K 197 N 195 I.

3i the same phase as in 1i is observed. It appears as a schlieren texture and is tentatively assigned an S_C phase. Even by supercooling, in none of these cases S_A phases were detected, e.g., 3e was cooled to 100°C (in contrast cf. 1e).

Comparison of all the benzoates of the four series 1 to 4 leads to the following general observations as expected: The clearing points of the alkoxy are higher than those of the alkyl derivatives and with increasing chain length the clearing points decrease. Furthermore, the clearing points of the cyclohexane derivatives are considerably below those of the benzene compounds, and again much lower clearing points are observed for the 1,4-dioxane components (Figure 3).

It may be assumed from these findings that the phases N, S_A or S_C are somewhat predetermined by the basic structural requirement of three rings and two ester functions. The temperature range for these phases, however, seems to be dependent on the type of the central ring structures.

An S_A phase could be observed for 1e. This compares to the known benzene compound 4d[15] [see also the related 1-(4-ethoxybenzyl)-4-(4-methylbenzoyl)hydroquinone: K 174 (S_A 123) N 277 I[16]] the smectic phase of which we assume to belong to the S_A type. Similarly, the cyclohexanes 3 should exhibit S_A phases if the melts could be undercooled sufficiently. In the case of 4i[17] and 4h[17] we suppose the smectic phases to be of the S_C type in relation to the S_C phase of 1,4-*bis*-(4-*n*-nonylbenzoyloxy)benzene (K 112 S_C 119 N 153 I).[18]

Owing to the preferred 1,4-*trans* diaxial conformation in the 1,4-dioxanes 1 these show less favorable liquid crystalline properties than the corresponding cyclohexanes 3 in which the *trans* diequatorial diesters predominate. Such a feature may be related to the increased spatial requirement in rotating the diaxial conformer of a 1,4-*trans*-substituted saturated six-membered ring compound, in contrast to the corresponding diequatorial conformer. This applies in particular to nematic phases; the smectic phases, however, are comparatively less destabilized. Obviously the cross-dipole moments[19] exerted by the 1,4-dioxane rings are of advantage for the stability of smectic phases.

In the 1,4-dithianes 2, largely the same conformations as in 1 are observed, but no mesomorphic phases whatsoever could be detected. Although here the central hetero ring system is somewhat stretched in comparison to cyclohexane, the bond angles are virtually identical. Thus steric reasons for this behavior are not at hand and other electronic or stereoelectronic features may be responsible.

CONCLUSIONS

In aliphatic six-membered ring compounds chair conformations with only equatorially-disposed substituents were discussed in the previous literature.[4,20] This study gave clear evidence that chair conformations with axially-disposed substituents occur and contribute considerably to the mesomorphic properties. Thus the clearing points of all cyclohexane derivatives as well as those of the corresponding oxygen heterocycles were supposed to be dependent on the conformer equilibrium and the contribution to the mesomorphic properties of the individual conformers. For the first time in dioxanes, the pure diaxial conformers could be studied, and

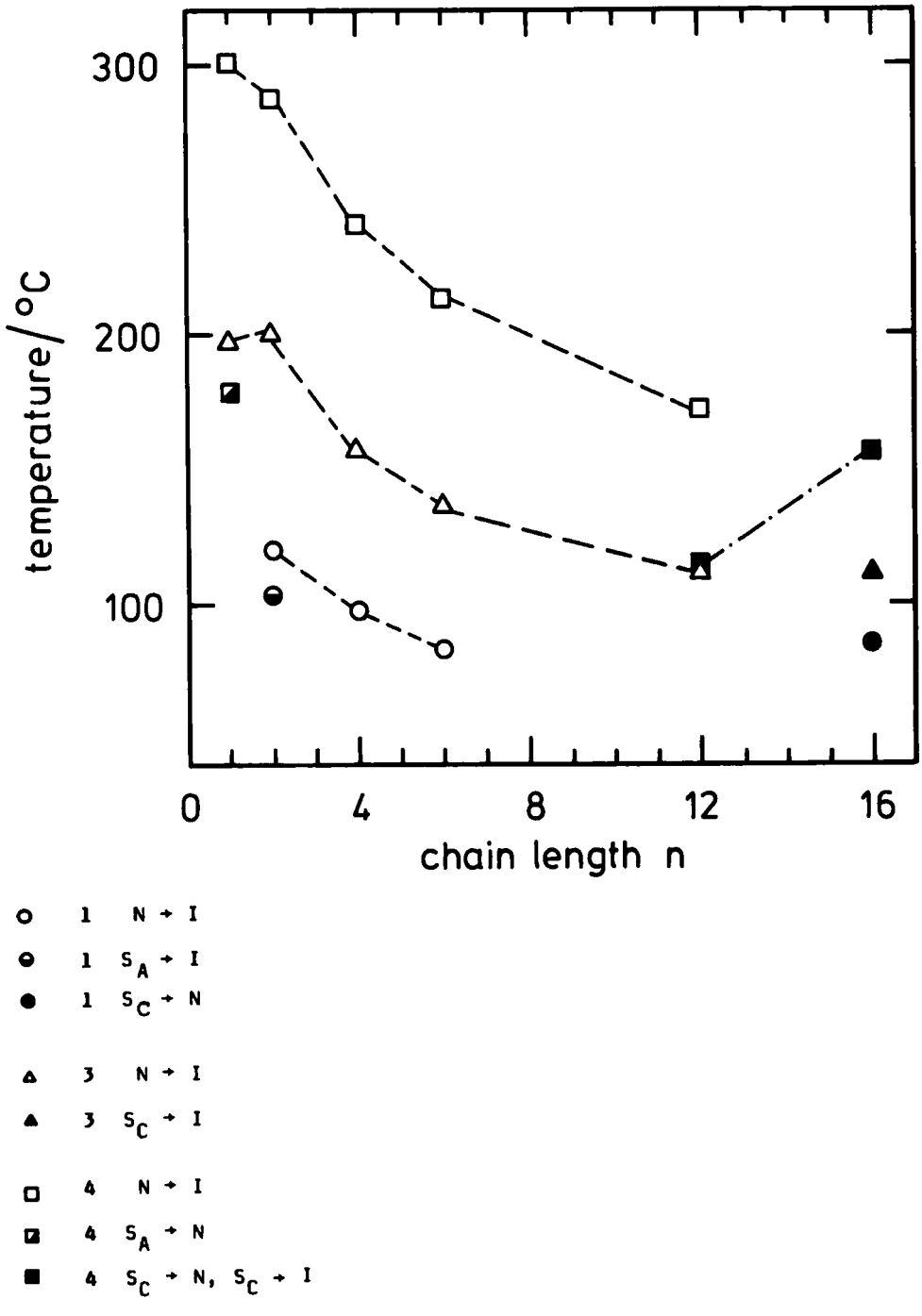


FIGURE 3 Plot of transition temperatures against number of carbon atoms in the alkoxy chain of compounds d–i in the series 1, 3, and 4.

proven to be mesomorphic as the diequatorial conformers. However, they exhibited considerably lower clearing points.

EXPERIMENTAL

Reactions were generally followed by thin layer chromatography on silica-gel foils 60 F_{254} (Merck). Detection was by UV absorption and/or spraying with 10% sulfuric acid in ethanol with subsequent heating (180°C). Column chromatography was on silica gel 60 (Merck) with the eluents given. Melting points and transition temperatures were determined on a Kofler heating microscope with polarizing filter equipment, and are corrected. ^{1}H NMR spectra were recorded on a Bruker WM-300 (300 MHz) in deuterochloroform with TMS as internal standard. For all series, the esterification is described and for the first members in detail. The structural features and the purity of all the other compounds were extensively checked by ^{1}H NMR spectroscopy and combustion analyses. These data are available, cf. Reference 5.

trans-*2,5*-Bis-*(4-methylbenzoyloxy)-1,4-dioxane (1a).* 4-Methylbenzoyl chloride (1.0 ml, 1.17 g, 7.57 mmol) is dissolved in dry pyridine (10 ml) and under exclusion of moisture, stirring, and ice cooling treated with 2,5-dihydroxy-1,4-dioxane (45 mg, 3.75 mmol). The solution is kept at room temperature overnight, and the solvents are evaporated. After three coevaporations with toluene, the remaining material is purified by column chromatography (chloroform), and recrystallized from ethanol. Yield: 450 mg (34%), m.p.: 204.5°C; ^{1}H NMR: δ = 2.42 (s, 6H, CH_3), 6.24 (d, 2H, H-2), 3.84 (d, 2H, H-3a), 4.40 (dd, 2H, H-3e), 8.02 (mc, 4H, o-H), 7.27 (mc, 4H, m-H); $J_{2,3e}$ = 1.4, $^2J_{3a,3e}$ = 12.5 Hz. Anal. calcd. for $C_{20}H_{20}O_6$ (356.4): C, 67.41; H, 5.66. Found: C, 67.24; H, 5.45.

Analogously prepared were:

trans-2,5-*bis*-(4-*n*-pentylbenzoyloxy)-1,4-dioxane (1b): 40%;
trans-2,5-*bis*-(4-methoxybenzoyloxy)-1,4-dioxane (1d): 39%;
trans-2,5-*bis*-(4-ethoxybenzoyloxy)-1,4-dioxane (1e): 35%;
trans-2,5-*bis*-(4-*n*-butoxybenzoyloxy)-1,4-dioxane (1f): 35%;
trans-2,5-*bis*-(4-*n*-hexyloxybenzoyloxy)-1,4-dioxane (1g): 13%;
trans-2,5-*bis*-(4-*n*-dodecyloxybenzoyloxy)-1,4-dioxane (1h): 28%;
trans-2,5-*bis*-(4-*n*-hexadecyloxybenzoyloxy)-1,4-dioxane (1i): 21%.

trans-*2,5*-Bis-*(4*-n-*pentylbenzoyloxy)-1,4-dithiane (2b).* 2,5-Dihydroxy-1,4-dithiane (290 mg, 1.90 mmol) and 4-*n*-pentylbenzoyl chloride (800 mg, 3.80 mmol) are reacted and worked up following the procedure described for 1a. After column chromatography (chloroform), crystallization was from ethanol. Yield: 530 mg (56%), m.p.: 123°C; ^{1}H NMR: δ = 2.67 (t, 4H, α-CH_2), 1.63 (mc, 4H, β-CH_2), 1.32 (mc, 4H, γ-CH_2), 1.31 (mc, 4H, δ-CH_2), 0.88 (t, 6H, ω-CH_3), 6.11 (dd, 2H, H-2), 2.96 (dd, 2H, H-3a), 3.88 (dd, 2H, H-3e), 8.06 (mc, 4H, o-H), 7.28 (mc, 4H, m-H); $J_{\alpha,\beta}$ = 7.8, $J_{\delta,\omega}$ = 6.7, $J_{2,3a}$ = 4.4, $J_{2,3e}$ = 1.2, $^2J_{3a,3e}$ = 14.5 Hz. Anal. calcd. for $C_{28}H_{56}O_4S_2$ (500.7): C, 67.16; H, 7.25. Found: C, 66.91; H, 7.16.

Analogously prepared were:

trans-2,5-*bis*-(4-methoxybenzoyloxy)-1,4-dithiane (2d): 81%;
trans-2,5-*bis*-(4-ethoxybenzoyloxy)-1,4-dithiane (2e): 89%;
trans-2,5-*bis*-(4-*n*-hexyloxybenzoyloxy)-1,4-dithiane (2g): 51%.

trans-*1,4*-Bis-*(4-methylbenzoyloxy)-cyclohexane (3a).* *trans*-Cyclohexane-1,4-diol (220 mg, 1.92 mmol) and 4-methylbenzoyl chloride are treated following the procedure described for 1a.

After workup and column chromatography (chloroform) crystallization is effected from ethanol. Yield: 640 mg (95%), m.p.: 173.5°C; ^{1}H NMR: δ = 2.40 (s, 6H, CH_3), 5.13 (mc, 2H, H-1), 1.77 (mc, 4H, H-2a), 2.13 (mc, 4H, H-2e), 7.93 (mc, 4H, o-H), 7.23 (mc, 4H, m-H). Anal. calcd. for $C_{22}H_{24}O_4$ (352.4): C, 74.98; H, 6.86. Found: C, 74.69; H, 6.70.

Analogously prepared were:

trans-1,4-*bis*-(4-*n*-pentylbenzoyloxy)-cyclohexane (3b): 83%;
trans-1,4-*bis*-(4-*n*-octylbenzoyloxy)-cyclohexane (3c): 82%;
trans-1,4-*bis*-(4-methoxybenzoyloxy)-cyclohexane (3d): 85%;
trans-1,4-*bis*-(ethoxybenzoyloxy)-cyclohexane (3e): 96%;
trans-1,4-*bis*-(4-*n*-dodecyloxybenzoyloxy)-cyclohexane (3h): 18%;
trans-1,4-*bis*-(4-*n*-hexadecyloxybenzoyloxy)-cyclohexane (3i): 80%.

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