

LIQUID-CRYSTALLINE BEHAVIOUR OF 2,5-DISUBSTITUTED 1,3-DIOXANES
SUBJECT TO THE FLEXIBILITY OF TERMINAL CHAINS

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(Received in Germany 4 November 1987)

Abstract: The liquid-crystalline behaviour of 2,5-disubstituted 1,3-dioxanes with the 5-substituents $-\text{CH}_2\text{CH}_2\text{CH}_3$, $-\text{OCH}_2\text{CH}_3$, $-\text{SCH}_2\text{CH}_3$ has been subjected to the intramolecular flexibility of these substituents, which is increasing in the given series to distort the rod-like arrangement of these species in the mesophase.

Trans-2,5-disubstituted 1,3-dioxanes usually emphasize wide ranges of mesophases¹. Especially if these compounds have alkoxy and alkylthio substituents in position 5, then, due to the strongly preferred diequatorial arrangement^{2,3}, very useful mesophase behaviour is expected.

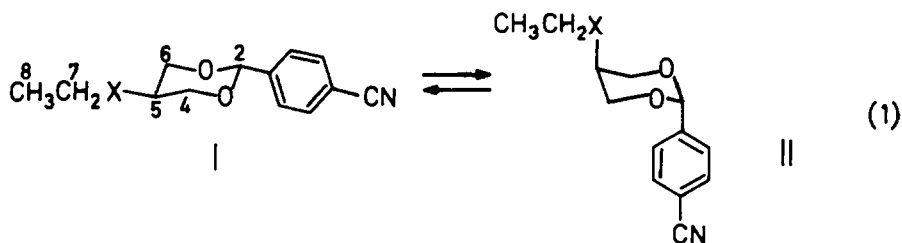
The studied 1,3-dioxanes have been prepared from the adequately 2-substituted propane-1,3-diols by acidic catalyzed acetalization with the corresponding aldehydes¹. The 2-alkoxy-propane-1,3-diols, necessary therefore, have been obtained from 2-phenyl-5-hydroxy-1,3-dioxane and alkylbromides by Williamson's ether synthesis and final deacetalization⁴; the corresponding 2-alkylthio-propane-1,3-diols, on the other hand, are readily available from the 2-alkylthiomalonic acid diethylesters by reduction with LiAlH_4 ³.

The compounds, together with the temperatures characterizing their liquid-crystalline behaviour, are collected in Table 1.

When comparing now the 5-alkyl substituted derivatives with the adequate 5-OAlk, and 5-SAlk substituted 1,3-dioxanes, dramatical clearing temperature[⊗] depressions (between 20 and 90 degrees) have been obtained, being strongest in the 5-SAlk derivatives. To find a reason therefore is the major objective of the following investigations.

First, in having a look on possible conformational sources (owing to the participation of the a,a-conformer II beside the e,e-invertomer I in (1)) the chemical equilibration⁵ of three model compounds 1 ($\text{X}=\text{CH}_2$), 2 ($\text{X}=\text{O}$), and 3 ($\text{X}=\text{S}$) has been studied; simple low temperature NMR studies of the single trans-isomer failed due

⊗) clearing temperature - temperature for the transition from the liquid-crystalline to the isotropic liquid state.



to the very preferred e,e-conformer I. The free conformational energies, ΔG° , which have been obtained after chemical equilibration in ether for six days are as follows:

5-substituent:	$-\text{CH}_2\text{CH}_2\text{CH}_3$	$-\text{OCH}_2\text{CH}_3$	$-\text{SCH}_2\text{CH}_3$.
$-\Delta G^\circ$ (kJ/mol):	4.23	5.96	7.64

and display increasing preference of the diequatorial conformer I in this series. If the clearing temperature is a function of ΔG° (e. g. the rod-like e,e-conformer favours the mesophase formation) the adequately increasing clearing temperatures would be expected. The experimental results of the Table 1, however, show divergent liquid-crystalline behaviour.

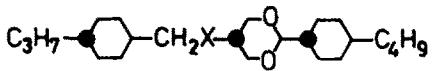
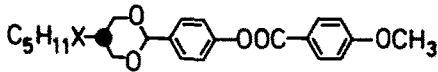
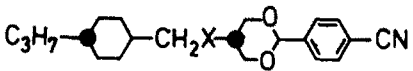
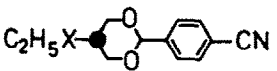
Second, to investigate the intramolecular flexibility of the 5-substituents, which obviously is also of influence on the distortionless rod-like arrangement in the mesophase, we measured the spin-lattice relaxation times T_1 of the carbon atoms in compounds 1-3 - given in Table 2. Additionally, after determining the NOE's and estimating the contributions of the dipole-dipole relaxation mechanism to the obtained T_1 's (between 65 % and 90 %) herefrom, the effective molecular correlation times τ_c have been calculated and included into Table 2. When comparing the corresponding relaxation parameters of the carbon atoms along the 5-substituents, the results are as follows:

5-substituent:	$-\text{CH}_2\text{CH}_2\text{CH}_3$	$-\text{OCH}_2\text{CH}_3$	$-\text{SCH}_2\text{CH}_3$
T_1 (s) :	2.44 2.92	3.23 3.24	5.31 5.11
τ_c (10^{-12} s $^{-1}$):	5.67 5.17	2.41 2.44	1.85 0.87

In the series $-\text{CH}_2\text{CH}_2\text{CH}_3 < -\text{OCH}_2\text{CH}_3 < -\text{SCH}_2\text{CH}_3$ the intramolecular flexibility of the 5-substituent is increasing. Even if this is controverse to the bond lengths in the case of $X=0$, it is in line with the obtained differences in the clearing temperatures of the adequately 2,5-disubstituted 1,3-dioxanes. In terms of these experimental results, the unexpected clearing temperature depressions of 2,5-disubstituted 1,3-dioxanes having OAlk and SAlk, respectively, as a 5-substituent result from the higher intramolecular flexibility of these substituents to distort the rod-like arrangement of the present species in the mesophase and to decrease the clearing temperature consequently.

Studies are on the way to make the obtained conclusions more general.

Table 1: Liquid-crystalline behaviour of 2,5-disubstituted 1,3-dioxanes¹⁾

Type	X	C	S _B	N	I	
	CH ₂	.20	.182	-	.	
	0	.51	.142	-	.	
	S	.2)	.135	-	.	
	CH ₂	.112	-	.197	.	
	0	.114	-	.176	.	
	S	.89	-	.142	.	
	CH ₂	.78	-	.183	.	
	0	.119	-	.149	.	
	S	.74	-	.94	.	
	<u>1</u>	CH ₂	.53	-	(.39)	.
	<u>2</u>	0	.140	-	-	.
	<u>2</u>	S	.105	-	-	.

¹⁾ C means crystalline solid; S_A, and S_B are smectic liquid-crystalline phases; N means a nematic phase; I describes the isotropic liquid.

²⁾ The transition from the solid to the smectic S_B mesophase could not be determined by polarized light microscopy.

Table 2: Spin-lattice relaxation times, T₁, NOE enhancement factors, η_C, partial dipole/dipole relaxation contribution, % DD, and the corresponding dipole/dipole relaxation times, T₁(DD); molecular correlation times, τ_C, obtained from % DD

compound	carbon atom	T ₁ (s) at 50 MHz	T ₁ (s) at 20 MHz	% DD ¹⁾	η _C ¹⁾	T ₁ (DD) (s) ¹⁾	τ _C (10 ⁻¹² s ⁻¹)
<u>1</u>	2	3.65	4.67	45.62	0.907	10.24	2.74
	4.6	1.90	2.12	45.32	0.901	4.68	6.00
	5	2.40	3.68	40.39	0.803	9.11	3.08
	7	2.44	3.32	67.00	1.332	4.97	5.67
	8	2.92	4.25	78.22	1.556	5.43	5.17
<u>2</u>	2	3.51	3.71	78.22	1.555	4.54	6.19
	4.6	1.87	2.25	87.79	1.944	1.93	7.27
	5	3.15	3.21	72.94	1.448	4.15	6.77
	7	3.23	5.05	76.56	1.522	5.84	2.41
	8	3.24	4.22	88.13	1.752	3.83	2.44
<u>2</u>	2	3.74	3.94	58.25	1.158	6.07	4.62
	4.6	1.78	2.35	82.70	1.644	2.82	4.92
	5	3.54	3.71	100	2.079	3.71	7.57
	7	5.31	4.94	65.14	1.295	5.83	1.85
	8	5.11	7.36	68.61	1.364	10.73	0.87

¹⁾ obtained at 20 MHz using a Bruker AC-80 NMR spectrometer.

EXPERIMENTAL

The ^1H NMR spectra have been recorded at 200.13 MHz and the ^{13}C NMR spectra at 50.67 MHz using a Bruker WP-200 NMR spectrometer. Temperatures have been calibrated to $\pm 1^\circ\text{C}$ using the involved temperature unit.

The trans-5-substituted 2-p-cyano-phenyl-1,3-dioxanes have been chemically equilibrated as follows: A drop BF_3 as a catalyst was added to 16 mg substance in 10 ml ether and the mixture hold constant at 25°C for six days in a sealed tube. Then the solvent has been removed, the reaction mixture worked up and ^1H NMR spectra recorded. The well separated absorptions of the tertiary protons in position 2 of the resulting cis/trans isomers have been integrated very carefully and finally used via $\Delta G^\circ = -RT \cdot \ln K$ to obtain the free conformational energies. The T_1 values (samples have been degassed several times under vacuum and the tubes sealed) have been obtained in inversion-recovery mode using the Bruker soft ware and the NOE's estimated quantitatively from the ^{13}C NMR spectra taken in inverse-gated mode. Herefrom the effective molecular correlation times τ_C are available in usual way⁶.

The phase transition temperatures were determined by crossed polarized light microscopy.

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