This article was downloaded by:
On: *26 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

New dimeric liquid crystals with chiral flexible spacers

J. Barberá[a]; A. Omenat[a]; J. L. Serrano[a]; T. Sierra[a]
[a] Química Orgánica, Facultad de Ciencias-I.C.M.A., Universidad de Zaragoza-C.S.I.C., Zaragoza, Spain

To cite this Article Barberá, J. , Omenat, A. , Serrano, J. L. and Sierra, T.(1989) 'New dimeric liquid crystals with chiral flexible spacers', Liquid Crystals, 5: 6, 1775 — 1782

To link to this Article: DOI: 10.1080/02678298908045687

URL: http://dx.doi.org/10.1080/02678298908045687

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 1989, VOL. 5, NO. 6, 1775–1782

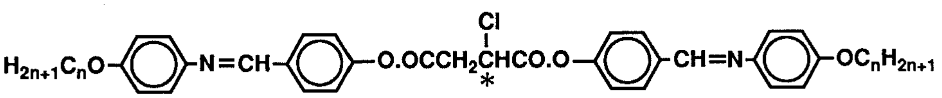
New dimeric liquid crystals with chiral flexible spacers

by J. BARBERÁ, A. OMENAT, J. L. SERRANO and T. SIERRA
Química Orgánica, Facultad de Ciencias-I.C.M.A.,
Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza, Spain

In order to obtain chiral compounds of low molecular weight expected to exhibit mesogenic and ferroelectric properties, the asymmetric carbon was introduced into the central part of the molecule. The series consists of nine chiral dimers in which the chiral flexible spacer derives from S-2-chlorosuccinic acid. The mesomorphic properties of the compounds were studied and all of them were found to be mesogenic. From $n = 6$ onwards the mesophases were chiral smectic C. Some analogous compounds derived from S-2-chloroglutaric acid were also prepared; these were not found to be mesogenic. The thermal instability of the 2-chlorosuccinic acid derivatives prevented the study of their ferroelectric properties. We attempted to perform this study for several mixtures involving 3-methyladipic acid derivatives and both 2-chlorosuccinic and 2-chloroglutaric acids derivatives. All the mixtures studied show chiral smectic C phases. The mixtures containing 2-chlorosuccinoyl derivatives show thermal instability; however those containing 2-chloroglutaroyl derivatives are stable, but do not show significant values of spontaneous polarization.

1. Introduction

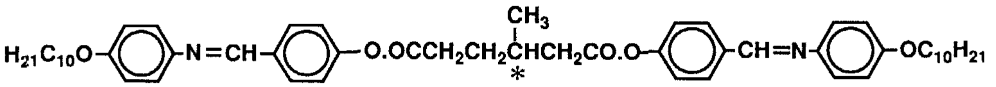
Until recently no liquid-crystalline compounds with the chiral centre in the central part of the molecule had been described [1]. Previously, we reported the mesogenic properties of a new series of chiral dimeric compounds derived from *R*-3-methyladipic acid [2]. All these materials were mesomorphic and many of them exhibited tilted smectic phases. However, in these compounds the dipole moment of the chiral centre is rather weak. In order to improve the ferroelectric properties of this type of material, we have synthesized other compounds in which the dipole at the chiral centre is stronger, this is the case of the C → Cl dipole [3]. The compounds described in this paper are bisazomethines containing the *S*-2-chlorosuccinoyl group as a central flexible spacer;



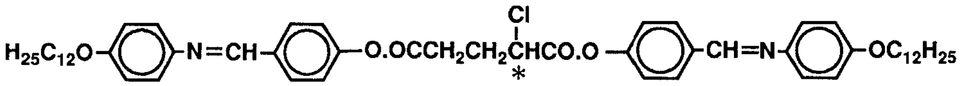
$n = 2,3,4,6,7,8,10,12,14$

For a better understanding of the influence of the flexible spacer on mesomorphism, some analogous compounds with an additional methylene group in the spacer, derived from *S*-2-chloroglutaric acid, have been synthesized and their potential liquid crystal properties investigated. In addition we prepared six binary mixtures of compounds of this type in order to obtain stable liquid crystal compositions so that their electric behaviour may be studied.

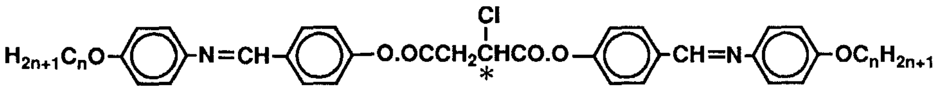
0267-8292/89 $3.00 © 1989 Taylor & Francis Ltd



A



B



n = 12, 14

C

Mixture	Components	Proportion
1	A–C (n = 14)	70:30
2	B–C (n = 12)	30:70
3	B–C (n = 12)	50:50
4	A–B	70:30
5	A–B	50:50
6	A–B	30:70

2. Experimental

The compounds described in this paper were prepared as shown in the synthetic scheme.

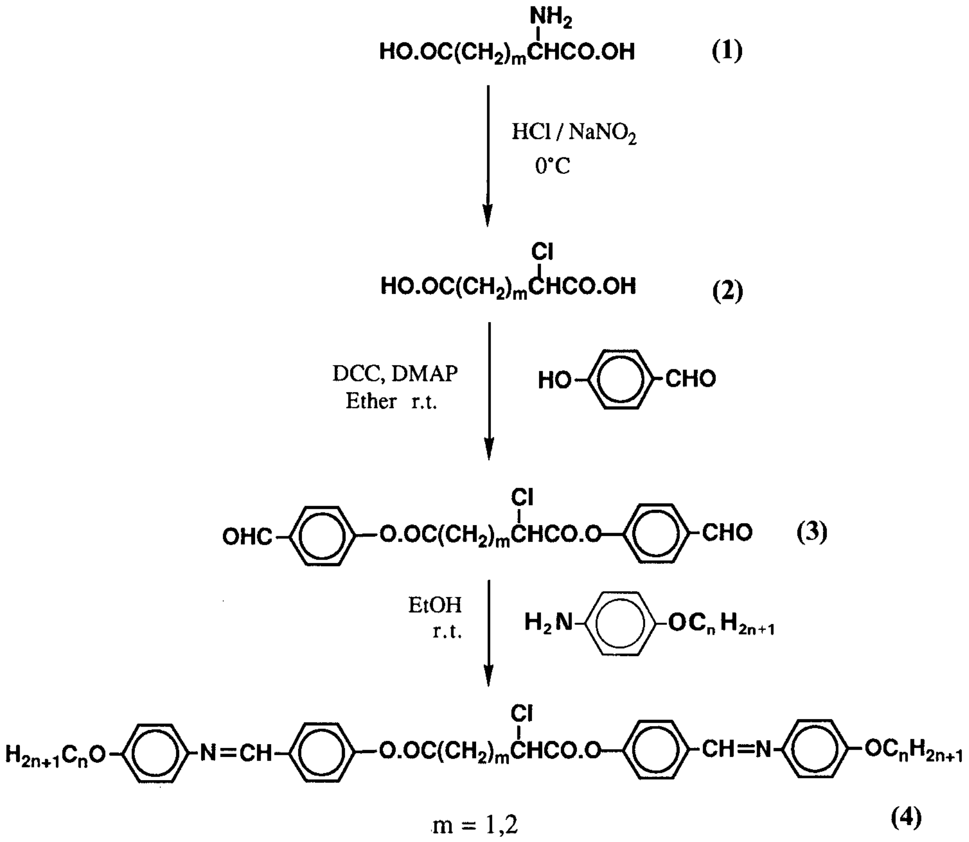
S-2-chlorosuccinic acid (**2**) was prepared from the corresponding α-aminoacid, L-aspartic acid (**1**), by reaction with sodium nitrite and chlorhydric acid, using the procedure reported by Fu *et al.* [4].

Bis-(4′-formylphenyl)-S-2-chlorosuccinate (**3**) was obtained by the esterification of S-2-chlorosuccinic acid (**2**) and 4-hydroxybenzaldehyde using DCC [5].

The final products (**4**) were prepared by condensation of (**3**) with the appropriate 4-alkoxyaniline in ethanol at room temperature. The purification of the crude materials obtained was by recrystallization from the appropriate solvent. The same procedure was performed in order to obtain the products with 2-chloroglutaroyl group as the flexible spacer, L-glutamic acid being the chiral starting material.

2.1. *Characterization*

The melting points, transition temperatures and enthalpies were determined using a Perkin–Elmer DSC-2 Differential Scanning Calorimeter. The heating rate was 10°C/min. The apparatus was calibrated by measuring the known melting point and heat of fusion of indium and tin. The optical observations were made using a Meiji polarizing microscope equipped with a Mettler FP-82 heating stage and a FP-80 central processor. The thermogravimetric analysis was performed in a Perkin–Elmer TGS-2 equipped with a System 4 Microprocessor Controller at a heating rate of 10°C/min under nitrogen. The identification of the products was carried out by the



Synthetic scheme.

usual spectroscopic methods; IR (Perkin–Elmer 783) and ^{1}H-N.M.R. (Bruker WP-80-SY) spectroscopy. The purity of all products was checked by the aforementioned techniques, by elemental analysis (C, H, N) using a Perkin–Elmer 240-C microanalyzer and by thin layer chromatography.

2.2. *Preparation of the mixtures*

All the mixtures were prepared using mechanical stirring. (*A*) In the isotropic phase for mixtures 4, 5 and 6 ($T \sim 205$°C). (*B*) In the mesophase for mixtures 1, 2 and 3, involving compounds **C** ($n = 12$ and 14) at 170–175°C to avoid their thermal decomposition.

3. Results and discussion

The transition temperatures, mesogenic properties and thermogravimetric data for 2-chlorosuccinic and 2-chloroglutaric acids derivatives are gathered in tables 1 and 2 respectively.

3.1. *Mesogenic behaviour*

Most of the members of the series show mesogenic behaviour. A chiral smectic C phase appears for the hexyl and higher homologues. A cholesteric mesophase is

Table 1. Transition temperatures and enthalpies and thermogravimetric data for the compounds derived from 2-chlorosuccinic acid.

n	Transition	*T*/°C	Δ*H*/kcal/mol	% weight loss†
2	C–Ch	193·8	14·03	
	Ch–decomposed	202†		5·0
3	C–decomposed	221†		4·25
4	C–decomposed	203†		5·0
6	C–S_I	184·1	6·00	
	S_I–S_{C^*}	189·0	1·87	
	S_{C^*}–decomposed	208†		5·0
7	C–S_I	176·9	7·26	
	S_I–S_{C^*}	189·4	2·77	
	S_{C^*}–decomposed	222†		3·0
8	C–S_I	173·0	8·19	
	S_I–S_{C^*}	184·9	2·60	
	S_{C^*}–decomposed	209†		3·0
10	C–S_I	162·8	8·66	
	S_I–S_{C^*}	173·1	2·89	
	S_{C^*}–decomposed	195†		4·0
12	C–S_I	155·6	10·96	
	S_I–S_{C^*}	171·6	2·48	
	S_{C^*}–decomposed	193†		2·95
14	C–S_I	150·6	12·54	
	S_I–S_{C^*}	164·6	2·29	
	S_{C^*}–decomposed	192†		2·9

† Data obtained by thermogravimetric analysis.

Table 2. Transition temperatures and enthalpies for compounds derived from 2-chloroglutaric acid.

n	Transition	*T*/°C	Δ*H*/kcal/mol
6	C–I	179·8	16·09
7	C–I	178·6	17·03
12	C–I	167·7	13·16

observed for $n = 2$. For $n = 3$ and $n = 4$, decomposition takes place on melting and therefore no mesophase can be observed. The six compounds which show a chiral smectic C phase ($n \geqslant 6$) also exhibit another tilted smectic phase at a lower temperature. In order to study the influence of the number of atoms in the chiral flexible spacer on mesogenic behaviour, we prepared three compounds derived from 2-chloroglutaric acid, in which the length of the spacer was increased by one methylene group. None of these showed mesogenic behaviour. This is not surprising if we consider that the all-trans conformation is the most stable for the chiral flexible spacer in the mesophase. Thus, in the case of an even number of atoms in the spacer the molecular structure is nearly linear, while for an odd number of atoms the structure is, on average, bent [6]. The results obtained for the 3-methyladipic acid derivatives (even number of atoms in the spacer) agree with this explanation [2].

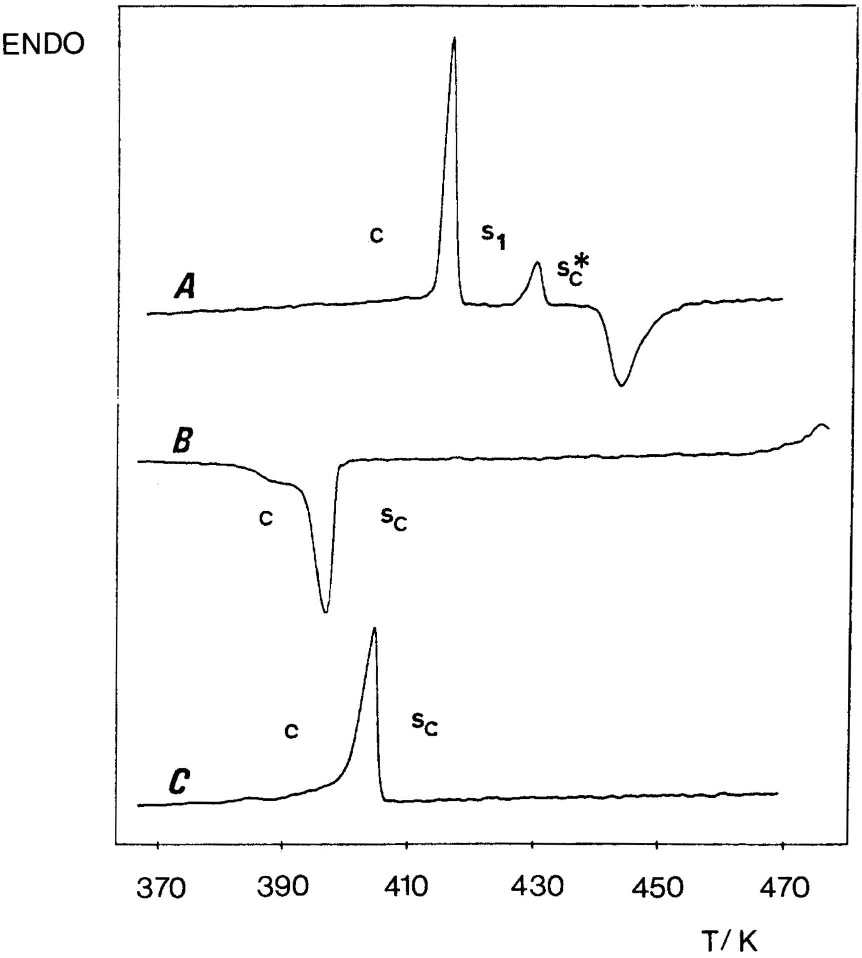


Figure 1. DSC thermograms for the tetradecyl homologue of the S-2 chlorosuccinoyl spacer series.

3.2. *Stability of the compounds*

By means of D.S.C. and optical microscopy it was observed that 2-chlorosuccinic acid derivatives decompose at about 200°C. By thermogravimetric analysis it was shown that all these compounds undergo a weight loss corresponding to HCl. The great stability of the final product, containing a highly conjugated double bond system explains this thermal decomposition. Figure 1 shows three typical thermograms for a 2-chlorosuccinic acid derivative. Thermogram A corresponds to the first heating scan, in which an exothermic peak corresponding to the decomposition process can be observed. Thermogram B was obtained for the cooling scan. Only one phase transition is observed which corresponds to the S_C–C transition. Thermogram C corresponds to the second heating scan in which the C–S_C transition is again detected.

The pure fumaric acid derivative ($n = 14$) was prepared and its thermal behaviour studied. The transition temperature T_{CS_C} agrees with that observed in Thermogram C. The transition S_C–I occurs at 546 K.

Table 3. Transition temperatures for the binary mixtures.

Mixture	Transition	*T*/°C
1	C–S_1	103·8
	S_1–S_{C*}	166·8
	(decomposed)	
2	C–S_{C*}	148·4
	(decomposed)	
3	C–S_{C*}	151·7
	(decomposed)	
4	C–S_1	106·4
	S_1–S_{C*}	144·0
	S_{C*}–I	176·9
5	C–S_1	142·5
	S_1–S_{C*}	151·9
	S_{C*}–I	167·1
6	C–S_1	145·4
	S_1–S_{C*}	155·2
	S_{C*}–I	166·9

In addition, the thermal stability of 2-chloroglutaric derivatives is higher than that for 2-chlorosuccinic derivatives and they do not lose weight in the thermogravimetric study below 250°C.

3.3. *Properties of the mixtures*

The optical and thermal results obtained for the six mixtures are gathered in table 3. Mixtures including 2-chlorosuccinoyl derivatives (1, 2 and 3) are still thermally unstable and it was not possible to reach the isotropic phase. However the mixtures including compounds **A** and **B** (4, 5 and 6) are thermally stable. Certain physical measurements were made on these mixtures with the resulting insignificant spontaneous polarization. These products, in spite of their purity determined by analytical methods, show a high conductivity. This may be attributed to the lability of the imine linkage when exposed to electric fields and at high temperatures.

3.4. *Phase identification*

The assignment of the mesophases relied mainly on optical microscopy.

3.4.1. *Chlorosuccinic acid derivatives—Pure compounds*

Cholesteric and smectic C phases were identified unambiguously. The cholesteric phase exhibited the typical oily-streaks texture and the smectic C phase showed schlieren and blurred schlieren textures. With regard to the schlieren textures, only centres with four derived brushes are observed which correspond to the smectic C phase [7].

Second smectic phase, S_1, appears at a lower temperature for these compounds. This phase is more viscous. We were able to prove that it is a tilted smectic phase since it is not possible to achieve the homeotropic texture by mechanical treatment. Figure 2 shows a microphotograph of this phase. A blurred-schlieren and a very fine

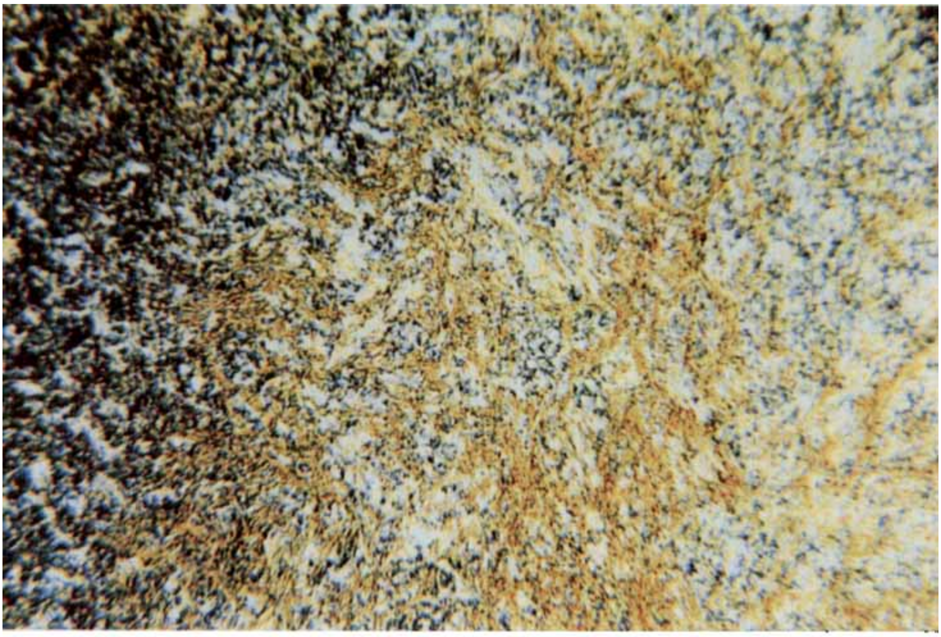


Figure 2.

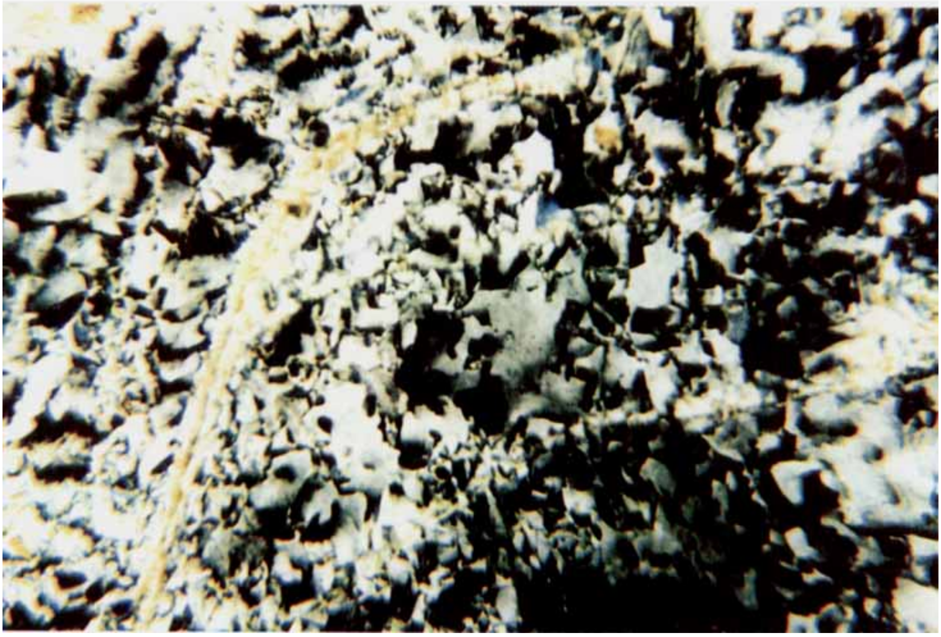


Figure 3.

mosaic textures (similar to that observed for certain S_F phases [7]) appear on cooling from the chiral smectic C phase.

3.4.2. *Mixtures*

All the mixtures show a smectic C phase, evident by the schlieren texture, on heating. In mixtures 4, 5 and 6, a focal-conic fan texture is observed on cooling from the isotropic liquid into the smectic C phase. Mixtures 1, 4, 5 and 6 also exhibit second more ordered smectic phase. The thermal degradation of Mixture 1 does not permit an exhaustive study of this phase. However, such a study is possible for Mixtures 4, 5 and 6. Figure 3 shows a mosaic texture formed on cooling the schlieren texture of the smectic C phase for Mixture 4. We conclude that this phase is the same as that observed in the pure compounds (S_1) despite its different texture.

4. Conclusions

We can conclude that, in general, compounds of this kind are good smectogens. In order to prepare compounds more suited to physical study, we propose (1) changing the linkage group in the mesogenic unit and (2) decreasing the transition temperatures by synthesizing non-symmetric dimers keeping the chiral group in the central spacer.

References

[1] Heppke, G., Lötzsch, D., and Oestreicher, F., 1987, *Z. Naturf.* (*a*) **42**, 279.
[2] Barberá, J., Omenat, A., and Serrano, J. L., 1989, *Molec. Crystals liq. Crystals*, **166**, 167.
[3] Goodby, J. W., and Leslie, T. M., 1984, *Liquid Crystals and Ordered Fluids*, Vol. 4.
[4] Fu, J., Birnbaum, S. M., and Greenstein, J. P., 1954, *J. Am. chem. Soc.*, **76**, 6054.
[5] Hassner, A., and Alexanian, V., 1978, *Tetrahedron Lett.*, **46**, 4475.
[6] Creed, D., Gross, J. R. D., Sullivan, S. L., Griffin, A. C., and Hoyle, C. E., 1987, *Molec. Crystals liq. Crystals*, **149**, 185.
[7] Gray, G. W., and Goodby, J. W. G., 1984, *Smectic Liquid Crystals. Textures and Structures.*