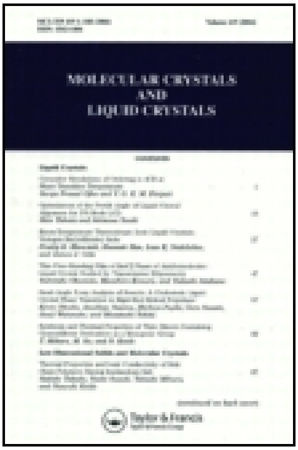

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Liquid Crystalline Thiadiazole Derivatives IV New Liquid Crystalline Materials With Broad Smectic C Ranges

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LIQUID CRYSTALLINE THIADIAZOLE DERIVATIVES IV
NEW LIQUID CRYSTALLINE MATERIALS WITH BROAD SMECTIC C RANGES

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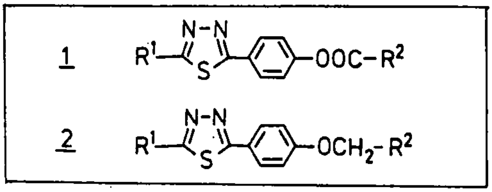
Abstract About 50 novel liquid crystalline 2,5-disubstituted 1,3,4-thiadiazole derivatives incorporating a carboxylic group or an oxymethylene unit have been prepared. The dependence of the liquid-crystal transition temperatures of this new class of compounds on diverse central linkages, chain lengths, alicyclic structural units and lateral substituents has been studied systematically. Most of the compounds exhibit broad smectic C mesomorphic ranges.

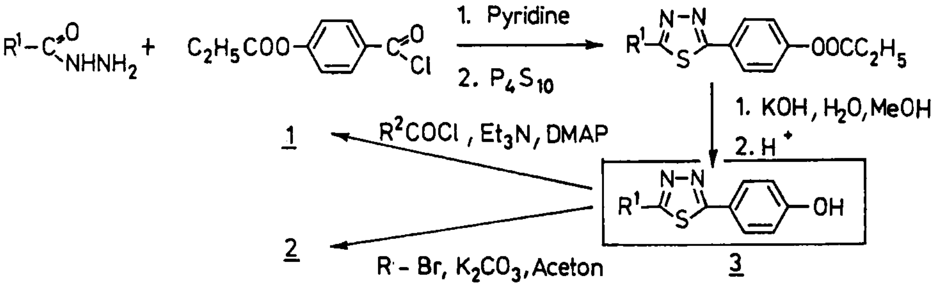
INTRODUCTION

Since the discovery of ferroelectricity in chiral smectic C phases by R. Meyer et al.[1] and its application in electro-optical displays proposed by Clark and Lagerwall[2], the search for new smectic C liquid crystals becomes important.
Recently it has been reported on several liquid crystalline thiadiazole derivatives[3-5]. These compounds exhibit broad smectic C ranges and possess moderate negative values of dielectric anisotropy.
These materials are useful components for S_C host mixtures to give ferroelectric liquid crystalline mixtures after addition of chiral dopants[6].
In order to obtain new materials with broad S_C ranges and also to study the influence of different structural units on the existence and the stability of the S_C-phases we have synthesized several novel 2,5-disubstituted 1,3,4-thiadiazole derivatives which belong to the general formulas 1 and 2.



SYNTHESIS

The preparations were achieved according to the following scheme.



Acylhydrazides were treated with 4-propionyloxybenzoylchloride, which serves as a protected 4-hydroxybenzoic-acid derivative, to give the 2-(4-propionyloxyphenyl)-thiadiazole derivatives after careful treatment with phosphorus pentasulfide in pyridine. Afterwards these compounds were deprotected by alkaline saponification to give the 2-(4-hydroxyphenyl)-thiadiazole derivatives 3. Further functionalizations were carried out using standard procedures. The samples were purified by flash chromatography and repeated recrystallization.

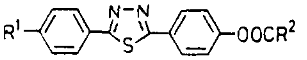
RESULTS AND DISCUSSION

All synthesized three ring compounds are mesogenic and most of them exhibit broad smectic C ranges. The phase transition temperatures were determined by microscopic observations, they are listed in the tables I - II.

The three ring compounds with only aromatic structural units exhibit the S_C phase over a broad temperature range. If the alkyl chains are not too long the S_C-phase is accompanied by the S_A phase and/or the nematic mesophase at elevated temperatures.

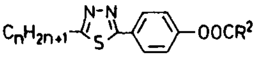
The clearing point of the laterally substituted esters 1.27 and 1.28 decreases with increasing size of the

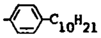
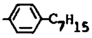
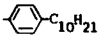
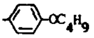
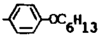
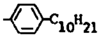
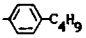
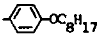
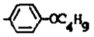
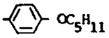
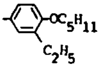
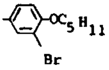
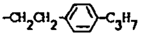
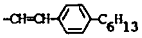
TABLE I



comp.	R^1	R^2	cr	S_X	S_C	S_A	N	is
1.1	$C_{10}H_{21}$	CH_3	. 117	- -	. 134	- -	. 183	.
1.2	$C_{10}H_{21}$	C_2H_5	. 107	- -	. 153	- -	. 181	.
1.3	$C_{10}H_{21}$	OC_4H_9	. 64	- -	. 146	. 147	. 166	.
1.4	$C_{10}H_{21}$	OC_7H_{15}	. 80	- -	. 153	- -	. 157	.
1.5	OC_5H_{11}	C_2H_5	. 118	- -	. 161	. 162	. 225	.
1.6	OC_5H_{11}	OC_4H_9	. 95	- -	. 141	- -	. 196	.
1.7	OC_8H_{17}	CH_3	. 116	- -	. 170	- -	. 213	.
1.8	OC_8H_{17}	C_2H_5	. 113	- -	. 169	- -	. 209	.
1.9	OC_8H_{17}	C_9H_{19}	. 90	- -	. 194	- -	- -	.
1.10	OC_8H_{17}	$CH(CH_3)C_8H_{17}$	. 65	(. 64)	. 135	- -	- -	.
1.11	OC_9H_{19}	OC_7H_{15}	. 83	- -	. 174	- -	. 183	.
1.12	OC_9H_{19}	OC_9H_{19}	. 94	- -	. 198	- -	- -	.
1.13	OC_9H_{19}	OC_4H_9	. 87	- -	. 168	- -	. 186	.

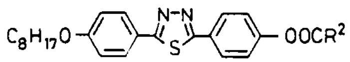
TABLE II

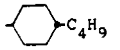
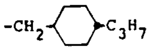
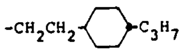


Comp.	n	R^2	cr	S_C	S_A	N	is
1.14	7	$-C_2H_5$	. 71	- -	- -	- -	.
1.15	9	$-C_2H_5$	. 62	- -	- -	- -	.
1.16	9	$-C_8H_{17}$	. 85	(.84.5)	- -	- -	.
1.17	5		. 104	. 121	. 135	. 146	.
1.18	7		. 108	. 132	- -	. 148	.
1.19	7		. 105	. 140	. 141	. 143	.
1.20	7		. 103	. 123	- -	. 181	.
1.21	7		. 92	. 149	- -	. 175	.
1.22	9		. 103	. 143	- -	- -	.
1.23	9		. 103	. 113	- -	. 149	.
1.24	9		. 98	. 166	- -	. 170	.
1.25	9		. 105	. 133	- -	. 173	.
1.26	9		. 94	. 144	- -	. 167	.
1.27	9		. 81	. 85	- -	. 99	.
1.28	9		. 79	. 131	- -	. 139	.
1.29	9		. 83	. 118	- -	. 146	.
1.30	9		. 95	. 152	- -	. 173	.

substituent. This effect is observed for the smectic C-nematic transition temperatures to a less extent. An interesting aspect of these results is the slightly broader smectic C mesophase range (52°) of the Br-substituted ester 1.28 compared to that (50°) of the related non-laterally substituted ester 1.26.
The introduction of a trans-1,4-cyclohexylidene unit into the alkyl chain of the ester 1.9 in such a way that the cyclohexane ring is linked with the substituted 2,5-diphenyl-1,3,4-thiadiazole rigid core by a nonlinear $-OOCCH_2-$ unit (comp. 1.32), only marginally affects the clearing point, while the melting temperature is significantly enhanced:

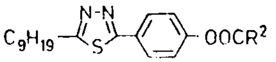
TABLE III

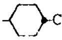
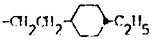
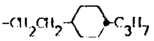
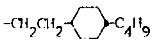


Comp.	R^2	cr	S_X	S_C	N	is
1.9	$-C_9H_{19}$	. 90	- -	. 194	- -	.
1.31		. 122	- -	. 232	. 297	.
1.32		. 130	- -	. 202	. 204	.
1.33		. 90	(·75)	. 216	. 249	.

Since the length of the terminal alkyl chain is reduced in this way, a nematic phase appears above the smectic C phase.
The nematic range is further increased by removing the methylene group or by the introduction of an additional methylene unit to give an even numbered spacer between the rigid core and the cyclohexane moiety (compounds 1.31 and 1.33 respectively). In this way the smectic C-nematic transition temperature is also increased whereas the melting pointsof the compounds 1.9 and 1.33 are essentially the same. Thus, it has been shown that the appropriate introduction of a trans-1,4-disubstituted cyclohexane ring into a n-alkyl chain could lead to a significant increase in the smectic C mesophase range. The same is true for the transition temperatures of the compounds 1.16, 1.34 - 1.38 summarized in table IV.
Inspection of this table indicates the appearance of some additional highly ordered liquid crystalline phases, which are smectic G phases in the cases of the $-OOCCH_2CH_2-$bridged compounds 1.36 - 1.38.

TABLE IV

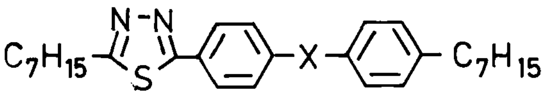


Comp.	R^2	cr	S_X	S_Y	S_G	S_C	S_A	N	is
1.16	$-C_8H_{17}$	. 85	- -	- -	- -	(·84,5)	- -	- -	.
1.34		. 81	. 87	. 98	- -	. 102	. 103	. 164	.
1.35		. 77	- -	- -	- -	. 81	. 89	- -	.
1.36		. 76	- -	- -	. 94	. 117	. 124	- -	.
1.37		. 83	- -	- -	. 105	. 112	. 130	- -	.
1.38		. 72	- -	- -	. 110	. 119	. 142	- -	.

The low temperature mesophases of the 4-butylcyclohexanecarboxylate 1.34 could not be determined by microscopic observations but differ from the S_G phase. These mesophases disappear with increasing length of the alkyl chain, attached to the cyclohexane ring (table V).

As another interesting fact the smectic C phase suddenly disappears and turns into a smectic B phase if a certain chain length (n = 7) is reached (comp. 1.42).

The S_B-phase is also formed if the cyclohexane ring is replaced by a 1,3-dioxane ring (comp. 1.45 and 1.46) If the carbonyl group of the cyclohexanecarboxylates is replaced by an oxymethylene group, neither a smectic C phase nor a smectic B phase could be detected. Contrary to this the S_C phase is not significantly influenced by this substitution in the case of the benzoic acid derivatives:

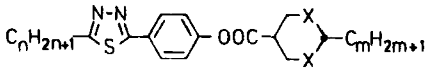


1.18 X = -OOC- cr 108 S_C 132 N 148 is

2.4 X = $-OCH_2-$ cr 95 S_C 124 N 140 is

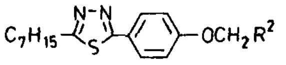
These observation again indicate the rather complex relationship between molecular structure and the kind of smectic aggregation observed.

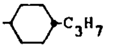
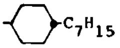
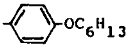
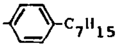
TABLE V



Comp.	n	x	m	cr	S_X	S_Y	S_G	S_B	S_C	S_A	N	is
1.39	7	CH_2	3	.95,5	- -	(. 88)	.99,5	- -	. 118	. 154	.174,5	.
1.34	7	CH_2	4	. 62	. 96	. 102	. 105	- -	. 110	. 165	. 173	.
1.40	7	CH_2	5	. 50	- -	- -	. 101	- -	. 105	. 173	. 176	.
1.41	7	CH_2	6	. 52	- -	- -	. 83	- -	. 126	. 159	. 166	.
1.42	7	CH_2	7	. 50	- -	- -	. 101	. 133	- -	. 173	- -	.
1.43	7	CH_2	8	. 62	- -	- -	. 94	. 134	- -	. 172	- -	.
1.44	9	CH_2	4	. 81	. 87	. 98	- -	- -	. 102	. 103	. 164	.
1.45	9	0	3	. 128	- -	- -	- -	. 139	- -	. 185	- -	.
1.46	9	0	7	. 110	- -	- -	- -	. 148	- -	. 180	- -	.

TABLE VI



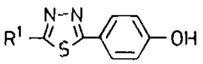
Comp.	R^2	cr	S_X	S_C	S_A
2.1		. 109	- -	- -	. 165
2.2		. 84	. 142	- -	. 160
2.3		. 108	. 117	. 156	- -
2.4		. 95	- -	. 124	. 140

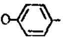
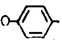
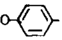
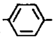
EXPERIMENTAL

2-Substituted 5-(4-hydroxyphenyl)-1,3,4-thiadiazoles

0,05 mol 2-substituted 5-(4-propionyloxyphenyl)-1,3,4-thiadiazole 1.2, 1.5, 1.8, 1.14 or 1.15 (obtained according to the general procedure given in[3,4]) is added to a solution of 5.5 g KOH in 200 ml methanol and 5 ml water. The resulting mixture is refluxed for 2 hrs. The solvent is evaporated at reduced pressure and the residue is dissolved in 250 ml water. The solution is acidified by addition of conc. hydrochloric acid. The resulting precipitate is succed of and recrystallized from ethanol to give the pure compounds 3:

TABLE VII Physical data of compounds 3.



Comp.	R^1	m.p. (°C)
3.1 [1]	C_7H_{15}-	104
3.2	C_9H_{19}-	97
3.3	$C_5H_{11}O$	194
3.4	$C_8H_{17}O$	172
3.5	$C_9H_{19}O$	193
3.6	$C_{10}H_{21}$	152

[1] ^{1}H-NMR (CDCl$_3$,ppm): 9.08 (1H, s,OH); 7.77 (2H,d,J = 8.7Hz, CH-arom.); 7.05 (2H,d,J = 8.7Hz, CH-arom.); 3.09 (2H,t,J = 7.5Hz, CH$_2$-thiadiazole); 1.87 - 0.84 (13H, m, CH-aliphat.)

^{13}C-NMR (CDCl$_3$,ppm): 168.7; 167.6; 160.0; 129.2 (2C); 120.9; 116.0 (2C); 31.1; 29.4; 29.3 (2C); 22.0; 13.8

2-Substituted 5-(4-acyloxyphenyl)-1,3,4-thiadiazoles 1

The trans-2-n-alkyl-1,3-dioxane-5-carboxylates 1.45 and 1.46 have been prepared by esterification of the trans-2-n-alkyl-1,3-dioxane-5-carboxylic acids with 3.2 using the EDC·CH$_3$I/DMAP procedure described in[7].
All other carboxylates have been obtained by esterification with acid chlorides using triethylamin as base and DMAP as catalyst[8].

Comp. 1.44: ^{1}H-NMR (CDCl$_3$, ppm): 7.93 (2H, d, J = 8.7Hz, CH-arom.); 7.17 (2H, d, J = 8.7Hz, CH-arom.); 3.10 (2H, t, J = 7.5Hz, CH$_2$-Thiadiazole); 2.57 (2H, d, J = 7.5Hz, CH$_2$-COO); 2.0 - 0.8 (38H, CH-aliphat.)

2-Substituted 5-(4-alkoxyphenyl)-1,3,4-thiadiazoles 2

Compounds 2.1 - 2.4 have been obtained by refluxing 5 mmol 3, 7 mmol of the appropriate alkylhalogenide and 10 g finely powdered anh. K$_2$CO$_3$ in 50 ml acetone for 12 hrs. After usual work up procedure the materials were recrystallized from methanol.

Comp. 2.3: ^{1}H-NMR (CDCl$_3$, ppm): 7.92 - 6.85 (8H, m, CH-arom.); 5.03 (2H, s, O-CH$_2$-ph); 3.96 (2H, t, J = 6.2Hz, CH$_2$-O); 3.10 (2H, t, J = 7.5

Hz, $C\underline{H}_2$-thiadiazole); 2.0 - 0.8 (24H, m, CH-aliphat.)

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