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Influence of molecular structure on the liquid-crystalline properties of 1,5-dihetero-spiro[5.5]undecane- and -dispiro[5.2.5.2]hexadecane derivatives

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Influence of molecular structure on the liquid-crystalline properties of 1,5-dihetero-spiro[5.5]undecane- and -dispiro[5.2.5.2]hexadecane derivatives

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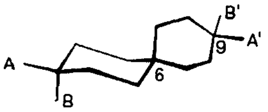
The synthesis and liquid-crystalline properties of 1,5-dioxa- and 1,5-dithia-spiro[5.5]undecane, 7,16-dioxa-dispiro[5.2.5.2]hexadecane and 1,5,10,14-tetraoxa-dispiro[5.2.5.2]hexadecane derivatives are described. The effects of terminal substituents and molecular structure on the liquid-crystalline properties of these materials are discussed.

1. Introduction

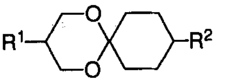
This paper describes the continuation of our previous studies of the synthesis of new liquid-crystalline compounds with a crooked centre in the molecular structure [1]. Such molecules include the spiro compounds, for instance spiro[5.5]undecanes (I), in which there is a 90° twist in the long axis of the molecule, because the carbon atom 6 is sp^3 hybridized and both rings are twisted. In the case of substitution in the 3 and 9 positions the molecules can form the rod-like geometry, which is necessary for mesomorphic behaviour.



(I)

Three classes of liquid-crystalline spiro compounds are known. Karamysheva *et al.* [2] obtained liquid-crystalline 9-substituted spiro[5.5]undecane-3-carboxylates in a very expensive way. Chan *et al.* [3] have synthesized spiro[3.3]heptane-2-carboxylates and Calaminus *et al.* [4] dispiro[5.1.5.1]tetradecane-7,14-diones. Of course the clearing points were decreased in relation to the analogous liquid crystals containing saturated rings without spiro bonds, because the length/breadth ratio has also decreased.

The stereochemistry of the spiro[5.5]undecanes is well known [5]. Accordingly these compounds are, when A/B or A'/B' are different, chiral in the C_3, C_6, and C_9 positions. The separation of the enantiomers is experimentally not possible [5]. We took as a model class of spiro compounds, i.e. 1,5-dihetero-spiro[5.5]undecanes for our investigations, because of their relative ease of synthesis:



1, 4, 5,

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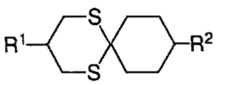
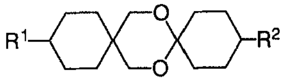
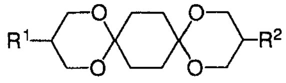


2, 6,



7

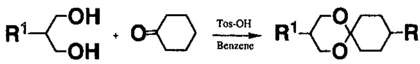


8

The stereochemical situation is the same in the heterocompounds as for the spiro[5.5]undecanes, but the bond angles and bond lengths are different and the barrier for ring inversion is lower.

2. Results and discussion

The preparation of 1,5-dihetero-spiro[5.5]undecanes is well established in the literature [6]. For instance, we obtained the following acids through the acid catalysed cycloacetalisation of substituted cyclohexanones with substituted 1,3-propanediols:



R^1 or R^2 = $-COOR$

It is possible to obtain the dithia- and thioxa-compounds in an analogous manner.

The alkyl- and cyclohexylalkyl-substituted dioxa- **1** and dithia-spirans **2** show enantiotropic liquid crystal phases with a smectic B/isotropic transition (see tables 1 and 2). Two homologous series of these compounds **1** do not show the usual alternation of the clearing points. When the molecules are longer, the transition temperature is increased (see figure 1). It is difficult to observe the transition from the crystalline to the smectic B phase by optical microscopy. The very clear ^{13}C N.M.R. spectra of the spiro compound **2.2** shows that the 3- and 9-substituents are in the equatorial position of the rings.

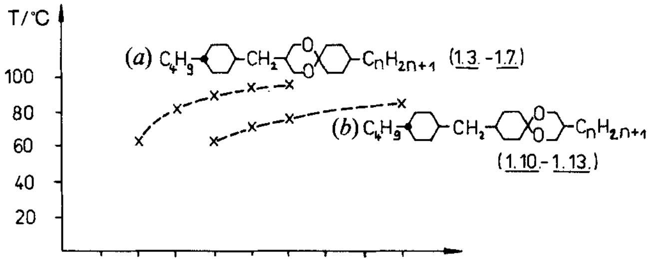
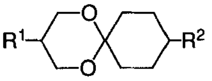
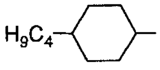
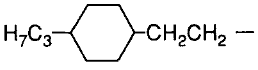
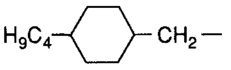
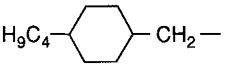
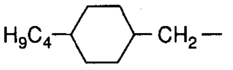
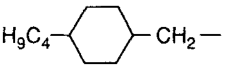
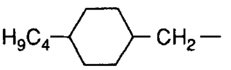
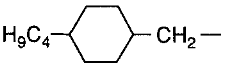
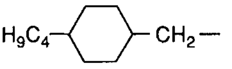
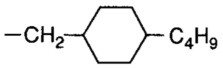
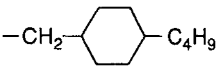
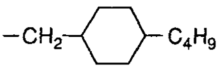
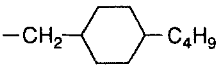
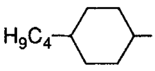
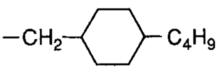
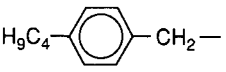
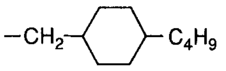
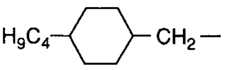
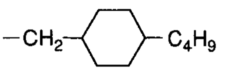
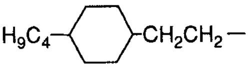
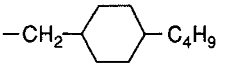


Figure 1. Clearing points (S_B–I) transition versus the number of carbon atoms (n) in the alkyl chain for the homologous series (a) and (b).

The comparison of the clearing points of the compounds listed in tables 1 and 2 yield two remarkable observations. First, replacement of the nonyl substituent in **1.13** and the octyl substituent in **2.1** by 4-butylcyclohexylmethyl in **1.16** and in **2.4**

Table 1. Transition temperatures (°C) of some 3,9-alkyl- and/or alkylcyclohexyl-1,5-dioxaspiro[5.5]undecanes **1**



	*R*¹	*R*²	C*		S_B		I
1.1		$-C_6H_{13}$	●	40	●	98	●
1.2		$-C_6H_{13}$	●	34	●	99	●
1.3		$-C_2H_5$	●	†	●	62	●
1.4		$-C_3H_7$	●	†	●	82	●
1.5		$-C_4H_9$	●	65 S_E 86	●	95	●
1.6		$-C_5H_{11}$	●	†	●	95	●
1.7		$-C_6H_{13}$	●	60	●	96	●
1.8		$-CN$	●	87	–		●
1.9		$-CH_2CH_2CN$	●	83	(● 70)		●
1.10	H_9C_4-		●	†	●	62	●
1.11	$H_{11}C_5-$		●	†	●	70	●
1.12	$H_{13}C_6-$		●	40	●	76	●
1.13	$H_{19}C_9-$		●	†	●	84	●
1.14			●	< 60	●	174	●
1.15			●	†	●	59	●
1.16			●	†	●	171	●
1.17			●	< 60	●	168	●

† The observation of the crystalline smectic B transition temperatures by optical microscopy was very difficult. The melting points are therefore often lower than those given in the table.

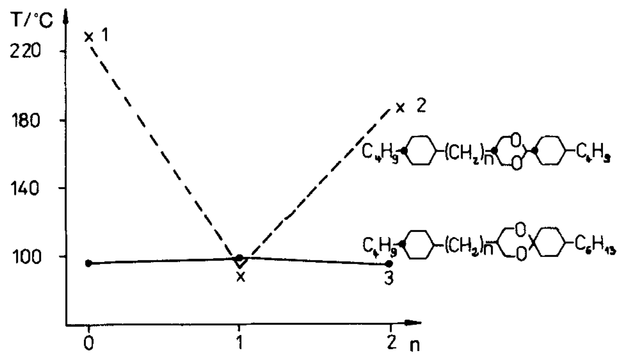
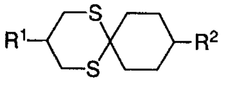
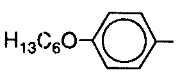
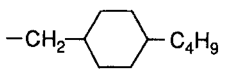
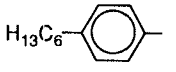
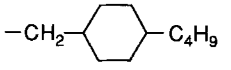
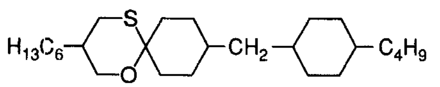


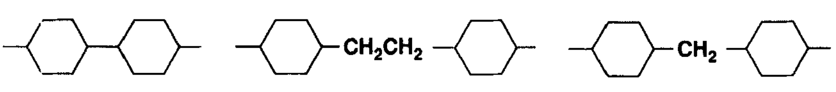
Figure 2. Comparison of the clearing points of the analogous cyclohexylalkyl-dioxanes [7] and dioxa-spiro-undecanes **1**: 1, C_6H_{13}–/C_6H_{13}–; 2, C_3H_7–/C_4H_9–; 3, C_3H_7–/C_6H_{13}–.

Table 2. Transition temperatures (°C) of some 3,9-disubstituted-1,5-dithia-spiro[5.5]undecanes **2** and one 1-thia-5-oxa-spiro[5.5]undecanes **3**



	R^1	R^2	K		S_B		I
2.1	$H_{13}C_6$—	—C_8H_{17}	●	22	●	(17)	●
2.2	$H_{13}C_6$—	—C_2H_5	●	20	●	(7)	●
2.3		—C_5H_{11}	●	45	●	46	●
2.4	$H_{13}C_6$—		●	60	●	113	●
2.5			●	70	●	114	●
3			●	20	●	119	●

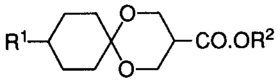
respectively leads to an increase in the clearing points by about 90–100 K. There are many other examples in the literature where a cyclohexylmethyl group in a terminal alkyl group has had the same effect on the transition temperature as a pentyl group (see the example in figure 3) [1]. On the other hand the clearing point of the *p*-butylphenylmethyl compound **1.15** is 112 K lower in comparison with that of compound **1.16**. Secondly, it is surprising to find that the clearing points of compounds **1.1**, **1.2** and **1.7** are similar since we normally find a decrease in clearing points along the series:

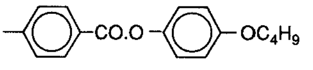
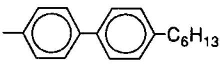
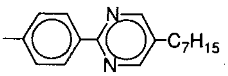
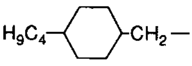
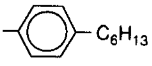
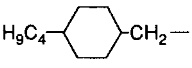
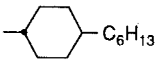
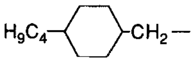
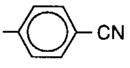
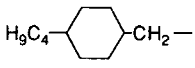
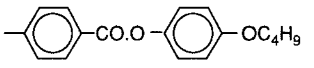
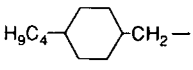
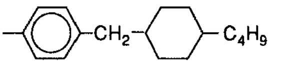
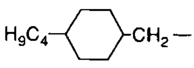
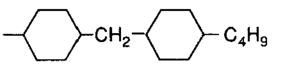
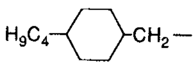
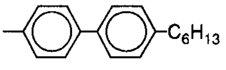
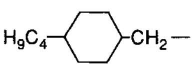
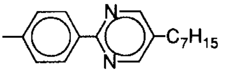


This fact is also true for compounds **1.14**, **1.16** and **1.17**. In figure 2 we can see the usual behaviour for the dioxane derivatives.

The reason for this unusual effect of the structure on the thermal stability of the mesophases lies in the crooked, rigid geometry of the spiro ring combination. The

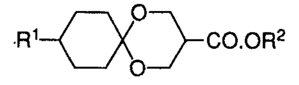
Table 3. Transition temperatures (°C) of 9-substituted-1,5-dioxa-spiro[5.5]undecan-3-carboxylates **4**

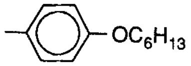
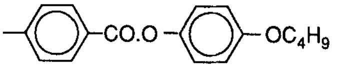
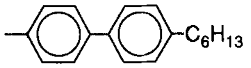
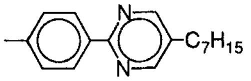
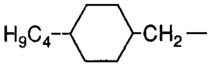
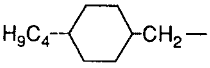
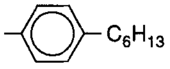
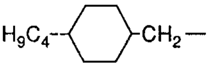
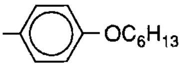
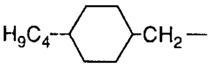
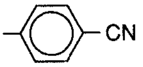
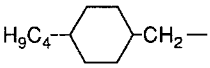
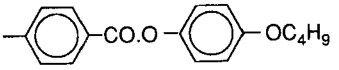
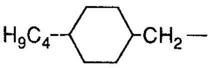
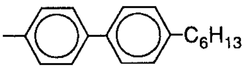
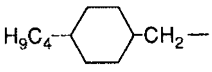
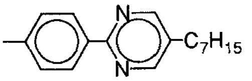


	R^1	R^2	C		S_B		S_A		N		I
4.1	$H_{13}C_6$—		●	108	●	138	–		●	141	●
4.2	$H_{13}C_6$—		●	116	●	133	–		–		●
4.3	$H_{13}C_6$—		●	90	●	103	–		●	115	●
4.4			●	97	●	110	–		–		●
4.5			●	95	●	159	–		–		●
4.6			●	126	●	(115)	–		–		●
4.7			●	88	●	152	●	168	●	207	●
4.8			●	117	●	(97)	–		–		●
4.9			●	115	●	174	–		–		●
4.10			●	120	●	192	–		–		●
4.11			●	127	–		–		●	178	●

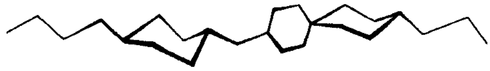
same effect is seen in the three series of esters of 1,5-dihetero-spiro[5.5]undecanes **4–6** given in tables 3–5. In figure 3 the clearing points of the different esters with alkylcyclohexylmethyl substituents (*a*, *b*) are about 80 K higher than those of the analogous alkyl substituted spirans (*d*, *e*). It is of interest to compare these results with the series (*f*), (*g*) and (*i*). The contribution of a cyclohexane ring in the butylcyclohexylmethyl compound (*f*) to the rigidity and linearity of the molecular structure is to increase the clearing point by 20 K compared to the nonyl compound (*g*). The clearing point of compound (*f*) is very similar to the cyclohexylmethyl-spirans (*a*, *b*). The alkyl substituted spirans (*c*, *d*, *e*) are also comparable with the lateral methyl substituted esters (*i*) which, because of the lateral methyl group have clearing points about 90 K below

Table 4. Transition temperatures (°C) of 3-substituted-1,5-dioxa-spiro[5.5]undecan-9-carboxylates **5**



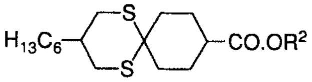
	*R*¹	*R*²	C	S_B	S_A	N	I
5.1	$H_{19}C_9$—		● 94	–	–	–	●
5.2	$H_{19}C_9$—		● 87	● 99	● 109	● 131	●
5.3	$H_{19}C_9$—		● 76	–	● 100	● 101	●
5.4	$H_{19}C_9$—		● 98	–	–	● 101	●
5.5		$-C_7H_{15}$	● 58	● (33)	–	–	●
5.6			● 79	● 89	–	–	●
5.7			● 128	● (94)	–	–	●
5.8			● 124	● (100)	–	–	●
5.9			● 144	● 158	● 164	● 207	●
5.10			● 122	–	● 158	● 169	●
5.11			● 139	–	–	● 169	●

that of compound (*f*). This methyl group has much the same effect on the transition temperatures as the spiro bond in the spiro[5.5]undecanes compared with bicyclohexyl compounds. We suppose that the relatively higher clearing points of (*a*) and (*b*) is caused by the combination of two crooked parts in the molecules, which allow a better rod-like geometry of the molecules in the mesophase (see structure II).



(II)

Table 5. Transition temperatures (°C) of 3-substituted-1,5-dithia-spiro[5.5]undecan-9-carboxylates **6**



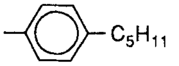
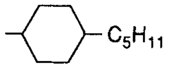
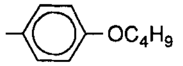
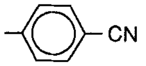
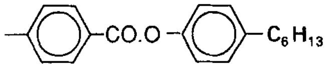
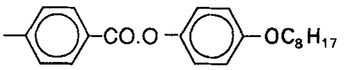
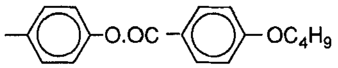
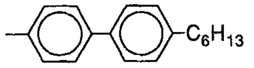
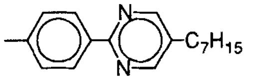
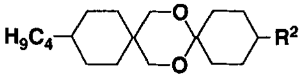
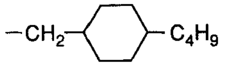
	*R*²	C		S		N		I
6.1		●	75	–		–		●
6.2		●	58	●	(47)	–		●
6.3		●	97	–		●	(30)	●
6.4		●	81	–		●	(29)	●
6.5		●	93	●	117	●	133	●
6.6		●	95	●	133	●	149	–
6.7		●	82	–		●	163	●
6.8		●	55	●	106	●	122	●
6.9		●	117	–		●	123	●

Table 6. Transition temperatures (°C) of 3,12-disubstituted-7,16-dioxa-dispiro[5.2.5.2] hexadecanes **7**



	*R*²	C		S_B		I
7.1	$-C_2H_5$	●	41	●	71	●
7.2	$-C_4H_9$	●	47	●	99	●
7.3	$-C_5H_{11}$	●	50	●	98	●
7.4	$-H_{13}C_6$	●	55	●	95	●
7.5	$-CH_2CH_2CN$	●	74	●	96	●
7.6	$-CH_2CH_2CO.OC_2H_5$	●	66	●	(55)	●
7.7		●	90	●	188	●

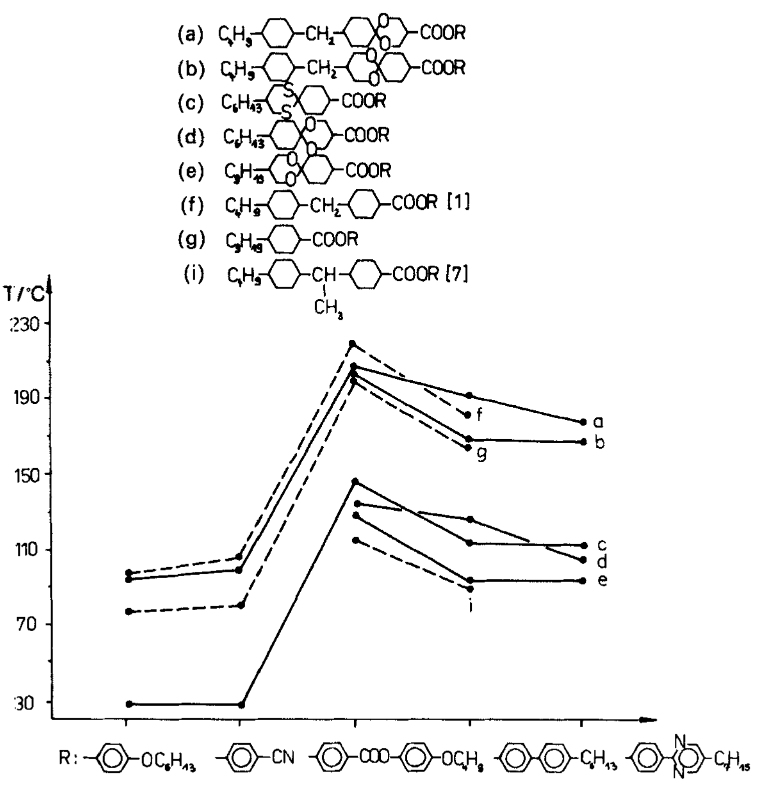


Figure 3. Comparison of clearing points of the analogous compounds **4–6**.

The tetraoxa-dispiro[5.2.5.2]hexadecanes **8** have much higher melting points than the dioxa-analogues **7** and in some cases higher clearing points (see **7.7** and **8.8** in tables 6 and 7). However we note the same result as before by comparing alkyl- and alkylcyclohexylmethyl substituted compounds **7.4** and **7.7**, **8.4–8.8** and **8.9**. The clearing points are increased by more than 90 K. The same is also true for the clearing temperature of the tetraoxa-tetraspiran **9**.

3. Experimental section

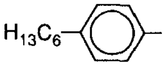
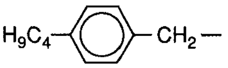
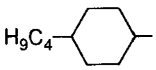
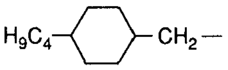
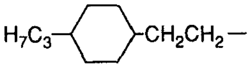
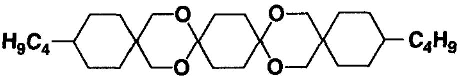
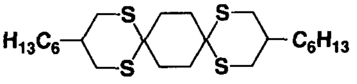
Melting points and transition temperatures were determined using a Boetius polarizing microscope (PHMK 05); ^{1}H N.M.R. and ^{13}C-N.M.R. were measured with Bruker AC 80 and Bruker WP 200 spectrometers. For H.P.L.C. we have used the HPP 4001 from the Laboratorni Pristoje Praha (C.S.S.R.). All new compounds have satisfactory infrared spectral properties and elemental analyses.

4-*n*-Alkylcyclohexanones and methylcyclohexan-4-one-carboxylate were synthesized by well-known methods [6]. The last step was an oxidation using pyridine chlorochromate (PCC) [8]. The substituted propan-diols and -dithiols have been described previously [9].

3.1. *Cycloacetalization*

4-*n*-Alkylcyclohexanones or 4-(4-*n*-butylcyclohexyl)methyl-cyclohexanones (3 mmol), 2-substituted propan-1,3-diol or -1,3-dithiol (3,3 mmol) and *p*-toluene sulphonic acid (50 mg) were refluxed in benzene (50 cm^3) for 2 hours in a water separator.

Table 7. Transition temperatures (°C) of 3,12-disubstituted-1,5,10,14-tetraoxaspiro[5.2.5.2] hexadecanes **8**

	R	C		S_B		I
8.1	H_9C_4—	●	110	–		●
8.2	$H_{11}C_5$—	●	117	–		●
8.3	$H_{13}C_6$—	●	112	–		●
8.4	$H_{19}C_9$—	●	101	●	115	●
8.5		●	203	–		●
8.6		●	140	–		●
8.7		●	188	●	235	●
8.8		●	178	●	208	●
8.9		●	145	●	207	●
9		●	170	●	211	●
10		●	163	–		●

After cooling the mixture was washed with water, $NaHCO_3$-solution (5 per cent) and water again, then dried over Na_2SO_4; the solvent was evaporated. The residue was purified by fractionated recrystallization from methanol or methanol/ethanol (3 : 1), until constant transition temperatures were obtained, the yield on pure spiro[5.5] undecanes (**1, 2**) was about 40 per cent. The same procedure was used to prepare 3-substituted methyl 1,5-dioxa (or dithia)-spiro[5.5]undecane-9-carboxylates and 9-substituted diethyl 1,5-dioxa-spiro[5.5]undecane-3,3-dicarboxylates. The crude or distilled esters were hydrolysed with KOH/methanol by refluxing.

3-substituted-1,5-dioxa-spiro[5.5]undecane-9-carboxylic acids were obtained from their potassium salts by acidification of the cooled and stirred ethylacetate solution with HCl (5 per cent) and by recrystallization from hexane: 3-(4-*n*-butylcyclohexyl)methyl- m.p.: 153–154°C, yield 73 per cent, 3-*n*-nonyl- m.p.: 65–66°C, yield 57 per cent. The 9-substituted-1,5-dioxa-spiro[5.5]undecane-3,3-dicarboxylic acids were decarboxylated (150°C; 2·7 kPa; 45 min) giving 9-substituted-1,5-dioxa-spiro[5.5]undecane-3-carboxylic acids, purified by recrystallization from hexane: 9-(4-*n*-butylcyclohexyl)methyl- m.p.: 156–160°C, yield 34 per cent, 9-*n*-hexyl- m.p.:

110–115°C, yield 29 per cent, where the yields relate to cycloacetalization. 3-*n*-Hexyl-1,5-dithia-spiro[5.5]undecane-9-carboxylic acid was obtained by simple acidification of the aqueous solution of its potassium salt and recrystallization from *n*-hexane: m.p.: 126°C, yield 90 per cent.

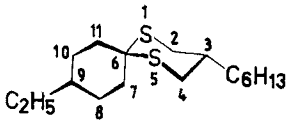
3.2. *Esterification* (*carbodiimid method*)

The pure acid (1 mmol), 4-substituted phenol or cyclohexanol (1 mmol), 1-(3-dimethylaminopropyl)-3-ethyl-carbodiimid methiodide (1·1 mmol) and 4-dimethylaminopyridin (10 mg) in dichlormethane (5 cm^3) were mixed at room temperature. After 20 hours the mixture was diluted with dichlormethane (15 cm^3), poured into water, washed with water, $NaHCO_3$-solution (5 per cent) and dried over Na_2SO_4. After removing the solvent the residue was recrystallized from ethanol, yielded about 90 per cent.

The structures of the products were verified using ^1H and ^{13}C N.M.R. as well as by I.R. spectroscopy. In addition, the elemental analysis of each compound is consistent with its proposed structure. The high purity of the final product (typically 97–99 per cent) was established using H.P.L.C. (R.P. column, methanol or hexanol as solvent).

3.3. *Examples of* ^{13}C *N.M.R. and* ^1H *N.M.R. spectroscopy*

3-*n*-hexyl-9-ethyl-1,5-dithia-spiro[5.5]undecane **2.2**



2.2.

(III)

^{13}C *N.M.R.* (50 MHz, $CDCl_3$):

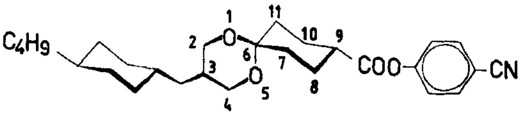
$C_{(3)}$: 38·9 ppm,

$C_{(9)}$: 35·6 ppm,

$C_{(6)}$: 50·2 ppm.

The values of $C_{(3)}$ and $C_{(9)}$ are in agreement with calculated values for equatorial substitution.

p-cyanphenyl 3-[4-*n*-butylcyclohexylmethyl]-1,5-dioxa-spiro[5.5]undecane-9-carboxylates **5.8**.



(IV)

^{1}*H-N.M.R.* (200 MHz, $CDCl_3$):

H^{9a}: 1 H; 2·6, 3 t [$J(8a9a) = J(10a9a) = 10$ Hz;
$J(8e9a) = J(10e9a) = 4$ Hz],

H^{2e}/H^{4e}: 2 H; 3·81, 2 d, [$J(2e2a) = J(4a4e) = 11$ Hz
$J(3a2e) = J(3a4e) = 4{\cdot}4$ Hz],

H^{2a}: 1 H; 3·57 t, [$J(2a2e) = J(2a3a) = 11$ Hz],

H^{4a}: 1 H; 3·48 t, [$J(4a4e) = J(4a3a) = 11$ Hz],

Phenylene-H: 7·67 ppm; 7·20 ppm.

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