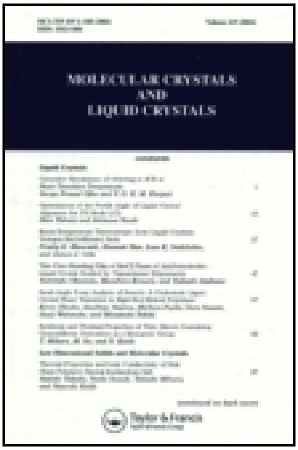

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Liquid Crystalline Esters of Alicyclic and Heterocyclic Acids[†]

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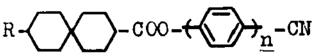
(Received December 9, 1982)

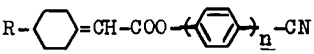
A number of new liquid crystalline esters containing spiro(5,5)undecane, cyclohexylidene, and pyrone fragments have been synthesized.

INTRODUCTION

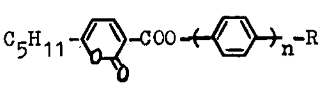
A program of work carried out in our laboratory has been devoted to the synthesis and to the study of the mesomorphic properties of various alicyclic and heterocyclic compounds.[1-4] Now we have obtained some new types of liquid crystalline esters described by the following general formulae:



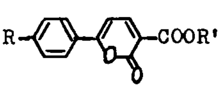
(I)



(II)



(III)



(IV)

[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 6–10, 1982.

wherein R = *n*-Alk, *n*-AlkO, CN
R′ = H, *n*-Alk
n = 1,2

It should be noted that the geometric structures of molecules I and II have never been realized in any other classes of liquid crystalline compound.

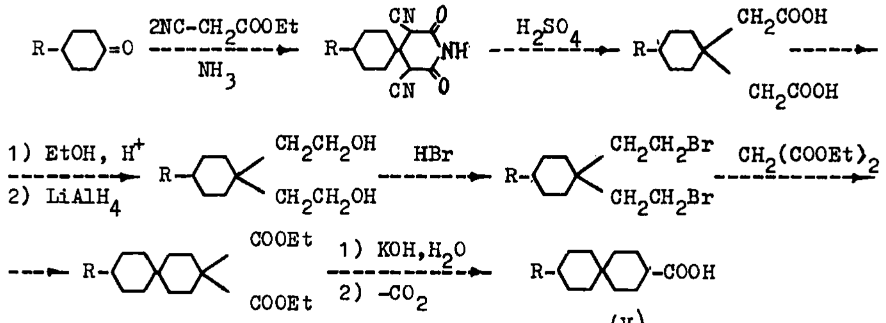
EXPERIMENTAL

Transition temperatures were measured using a Mettler-FP-52 heated stage used in conjunction with a polarizing microscope (MIN-8).

The proton coupled and decoupled carbon-13 magnetic resonance spectra were recorded (solvent: $CDCl_3$) using a Bruker-M-250 spectrometer. The chemical shift data were obtained with TMS (tetramethylsilane) added as reference.

The purity of the intermediate products was monitored by gas-liquid chromatography (capillary column, 50 m in length, packed with apiezon L; flame-ionization detector).

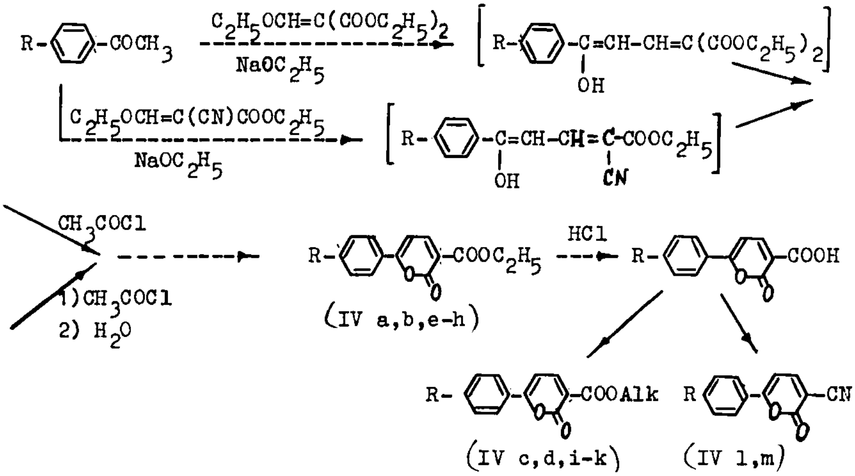
The starting 3-alkylspiro(5,5)undecane-9-carboxylic acids were prepared according to a procedure used for the methyl homologue.[5]



(V)

4-Pentyl-cyclohexylideneacetic acid (VI) was synthesized by dehydratation[6] of 4-pentyl-1-hydroxycyclohexyl-1-acetic acid obtained from 4-pentylcyclohexanone and methyl bromoacetate by the Reformatsky reaction.

The starting 3-carboxy-6-pentylpyrone-2 was prepared by known methods.[11] The esters (IVa, b, e–h) (*R*′ = C_2H_5) were obtained from 4-substituted acetophenones in the presence of sodium ethylate using two different condensation agents: ethoxymethylenemalonic ester[12] or ethoxymethylenecyanoacetic ester; subsequent cyclization by acetyl chloride leads to the compounds IV in yields of 30–50% in the first case and 10–35% in the second case. The cyclization of the intermediate product in the latter case was accomplished *via* the cyano-group instead of the carbethoxy group.

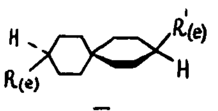


Hydrolysis of the ethylesters (IVa, b, e–h) led to the 3-carboxy-6-(4-alkyl(alkoxy)phenyl)pyrones-2; these were converted into acid chlorides and then to amides and nitriles (IVl, m) or esters (IVc, d, i–k).

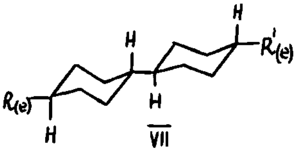
The esters (III) were prepared by the interaction of 3-carboxy-6-pentylpyrone-2 with 4-substituted phenols in benzene or toluene in the presence of phosphorus oxychloride. The other esters (I, II and IV) were obtained by standard procedures from phenols or alcohols and the corresponding acid chlorides. All of the synthesized compounds were recrystallized until constant transition temperatures were achieved. Satisfactory elemental analyses were obtained for all of these compounds. The transition temperatures of the compounds (I–IV) and, additionally, (V and VI) are listed in Table I.

RESULTS AND DISCUSSION

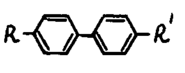
From a formal point of view, the structure of the 3,9-disubstituted spiro(5,5)undecanes is close to that of the liquid crystalline *trans*-4,4′-disubstituted bicyclohexyls[7] (VII) and of the biphenyls[8] (VIII):



V



VII



VIII

The main structural requirement for mesomorphism is known to be a linearity and an anisotropic geometric shape of the molecules. This criterion is realized absolutely in the linear and rigid biphenyls (VIII). Thanks

TABLE I

Transition temperatures of compounds (I–VI) (°C)

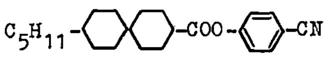
Index	*R*	Alkyl = *R'* in (IV)	*n*	T_{sm}	T_{nem}	T_{is}
Ia	CH_3	—	1	—	—	56
Ib	C_2H_5	—	1	—	—	86
Ic	C_4H_9	—	1	65	—	73
Id	C_5H_{11}	—	1	63	—	72
Ie	CH_3	—	2	—	96	162
If	C_2H_5	—	2	—	99	185
Ig	C_4H_9	—	2	81	150,	186
Ih	C_5H_{11}	—	2	87	163	178
IIa	C_5H_{11}	—	1	—	—	53
IIb	C_5H_{11}	—	2	75	110	134
IIIa	C_4H_9	—	1	—	—	82
IIIb	CN	—	1	—	—	116
IIIc	OC_4H_9	—	1	—	—	76
IIId	OC_6H_{13}	—	1	—	—	75
IIIe	CN	—	2	122	132	208
IVa	C_6H_{13}	C_2H_5	—	67	—	69
IVb	C_7H_{15}	C_2H_5	—	64	—	71
IVc	C_7H_{15}	C_4H_9	—	—	—	91
IVd	C_7H_{15}	$C_{10}H_{21}$	—	63	—	69
IVe	C_9H_{19}	C_2H_5	—	74	—	76
IVf	OC_4H_9	C_2H_5	—	82	—	104
IVg	OC_6H_{13}	C_2H_5	—	76	—	108
IVh	OC_9H_{19}	C_2H_5	—	80	—	113
IVi	OC_9H_{19}	C_3H_7	—	84	—	115
IVj	OC_9H_{19}	C_4H_9	—	76	—	102
IVk	OC_9H_{19}	$C_{10}H_{21}$	—	74	—	102
IVl	OC_6H_{13}	CN	—	—	—	95
IVm	C_7H_{15}	CN	—	—	—	92
Va	CH_3	—	—	—	—	90
Vb	C_2H_5	—	—	—	—	77
Vc	C_4H_9	—	—	—	—	78
Vd	C_5H_{11}	—	—	—	—	66
VI(amide)	C_5H_{11}	—	—	—	—	120

to the diequatorial substitution of the cyclohexane rings in the molecules of the *trans*-4,4'-disubstituted bicyclohexyls (VII), the geometric shape anisotropy required to provide the mesomorphic properties is also ensured. The two cyclohexane rings in the spiro(5,5)undecane compounds are conjoined by the common atom and the orientation of the conjectural planes of the six-membered rings is close to perpendicular. It is not quite evident whether the geometry of such derivatives satisfies the main criterion for liquid crystals or not.

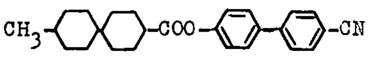
The first of the compounds synthesized—the 3-alkylspiro(5,5) undecane-9-carboxylic acids (V) did not happen to be mesomorphic. However, their carbon-13 magnetic resonance spectra indicated the equatorial substitution of the six-membered ring by the carboxyl group. The chemical shift for the carboxylic carbon atom was observed at δ 43.42 ppm relative to TMS (the carbon-13 chemical shift values of δ 44.5 ppm and δ 40 ppm were obtained for the equatorial and axial carboxyl groups respectively by earlier investigations of cyclohexanecarboxylic acid.[9,10]

Evidently the equatorial position of the carboxyl group in the compounds (V) is not enough to provide mesomorphic properties in the 3-alkylspiro(5,5)undecane-9-carboxylic acids in contrast to the 4-alkyl-*trans*-cyclohexane-1-carboxylic acids.[13] Further investigation of the molecular structure of the spiro-acids (V) is necessary.

The 3-alkylspiro(5,5)undecane-9-carboxylates (I) did however demonstrate liquid crystalline behavior (Table I). In the homologous series, there is an even-odd alteration, with the higher clearing points being found for the even homologues. We should note that phenyl carboxylates (Ic, d) show exclusively smectic properties, whereas with the biphenyl carboxylates (Ie–h), the introduction of the second benzene ring provides an increase in molecular conjugation and gives rise to an additional nematic phase. Therefore molecules of about equal length show quite different mesomorphic behavior:



Id: T_{sm}63°, T_{is}72°



Ie: T_{nem}96°, T_{is}162°

Thus the presence and the temperature range of the smectic mesophase in the compound of structure (I) are not provided only by the length (geometric shape anisotropy) but also by the relation between the saturated (nonpolarizable) and the aromatic (polarizable) parts. This conclusion is experimentally verified when we study the liquid crystalline 4-pentylcyclohexylideneacetates (II). The geometric structure of a 4-cyclohexylideneacetic acid (VI) is close to that of a spiro(5,5)undecane-9-carboxylic acid (V): the plane of the exocyclic double bond is perpendicular to the conjectural plane of the cyclohexane ring. Among the derivatives of acid (VI), 4-cyanophenyl carboxylate (IIa) does not exhibit mesomorphism; the biphenyl carboxylate (IIb) exhibits both smectic and nematic behavior. Comparing the transition temperatures of IIb with those of the spirane analogue (IH), one can see a decrease in the clearing point (about 44°C). This considerable decrease is evidently related to a deterioration of the linear, compact structure of the mesogenic molecule by the rigid exocyclic double bond. On the contrary, the introduction of the polarizable group $>C{=}CH{-}COO{-}$ to the molecule (IIb) leads to some broadening of the nematic temperature range compared with that for the ester (Ih) (the nematic ranges are 23°C and 15°C, respectively) and to a considerable decrease in the smectic temperature range (35°C and 76°C), respectively).

The hydrogenation of the double bond in 4-pentylcyclohexylidene-acetic acid causes complete disappearance of the nematic mesophase in the appropriate 4-cyanobiphenyl carboxylate, so that the smectic mesophase is only present within a narrow temperature range (65–69, 6°C).

Therefore the mesomorphic thermal stability of (IIb) decreases by 64°C due to the hydrogenation of the double in the cyclohexylidene fragment.

The above-mentioned mechanisms for the changes in the mesomorphic properties (i.e. in the type of mesophase and its temperature range) may be useful when constructing new liquid crystal materials containing the cyclohexane ring. We should also note that the use of spiro(5,5)undecane and cyclohexylidene derivatives as optical isomers could lead to chiral nematogens of a new type.

The derivatives of 3,6-disubstituted pyrones-2 are potentially interesting liquid crystal materials as they contain a permanent dipole moment due to the presence of the lateral carbonyl group. It may be expected therefore that the dielectric constants of the pyrone derivatives will differ strongly from those of the benzene analogues. As for the transition temperatures of the compounds (III), only the 4-cyanobiphenyl carboxylate (IIIi) demonstrates mesomorphic properties and forms both a smectic and a high temperature nematic mesophase. 4-Substituted phenyl carboxylates (IIIa–d) do not exhibit mesomorphism; they have higher melting points than the analogous derivatives of the 4-alkyl-benzoic acids.

The 3-carboalkoxy-6-(4-alkyl(alkoxy)phenyl)pyrones-2 (IV, R' = Alk) possess smectic mesophases; their transition temperatures are close to those of the analogous benzene analogues. The acids IV (R' = H) are not mesomorphic. This effect may be explained by the formation of an *intra*molecular hydrogen bond.

The dielectric constants of some cyano-derivatives (III, IV) were found by an extrapolation method using results obtained by measurements on their solutions in a mixture of azoxy compounds. Their dielectric anisotropy seems to be higher than that of the benzene analogues; for example: $\Delta\varepsilon = 29.1$ for (IIIb); $\Delta\varepsilon = 40.5$ for (IVl) ($R = C_6H_{13}O$, terminal CN); $\Delta\varepsilon = 30.2$ for IVm ($R = C_7H_{15}$, terminal CN).

Acknowledgment

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