10^{-11} sec.[11] Hence, even very low probability long range events become much more likely, and good signal intensity is obtained. This work suggests the possibility that a surface might be substituted for a collision gas as a convenient, simple and efficient method of exciting gaseous ions.

Acknowledgment We thank the National Science Foundation for its support of this work.

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Novel Stable Chiral Nematic (Cholesteric) Liquid Crystals

Sir:

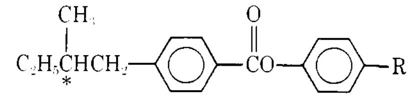
We wish to report the preparation of useful novel cholesteric liquid crystal materials possessing a combination of highly desirable properties: right-handed cholesteric type, very small optical pitch, and high chemical stability.

Liquid crystals with cholesteric properties have traditionally and most generally been based on the cholesteryl moiety.[1,2] In general, other optically active or chiral molecules with potential liquid crystal properties may also have a cholesteric mesophase. This type of cholesteric liquid crystal has also been called a chiral nematic liquid crystal.[3]

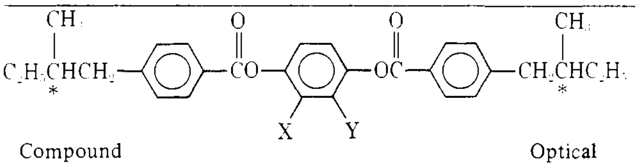
Examples of chiral nematic liquid crystals have been based on optically active 4-(2-methylalkoxy)biphenyl derivatives[4,5] and Schiff bases incorporating the optically active 2-methylbutyl group[6-10] or 1-deuteriobutoxy group.[11] These materials have large optical-pitch characteristics and/or are relatively unstable with respect to hydrolytic stability; in fact, the only materials known with small optical-pitch values are the hydrolytically unstable optically active 4′-alkoxybenzal-4-(2-methylbutyl)anilines (optical-pitch values ~0.35 μm), which have the optically active 2-methylbutyl group bonded directly to an aromatic ring without the intermediacy of an oxygen atom or other functionality.[3]

Our interest in and work with relatively stable ester-type liquid crystals,[12-14] led us to the investigation of optically active esters. We developed a synthesis for optically active 4-(2-methylbutyl)benzoyl chloride, which is obtained from the corresponding (+)-2-methylbutylbenzene[3] by means of a direct reaction with oxalyl chloride and aluminum chloride or via conversion of the alkylbenzene to the acetophenone, which is oxidized with hypochlorite to give the free acid. Simple phenyl benzoates as well as symmetrical and unsymmetrical phenylene diesters are prepared in the usual way[13,14] from reactions with phenols, hydroquinones, or 4′-substituted phenyl 4-hydroxybenzoates. We chose the optically active alkyl (rather than alkoxy) group because previous work[3] implied but did not show that this end group in general should favor chiral nematics with small optical-pitch values.

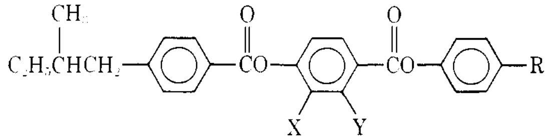
Table I. Chiral Nematic Esters



Compound no.	R	Mp, °C	Optical pitch, μm
1	C_3H_7	0	0.24
2	C_8H_{17}	−2	0.28
3	OCH_3	46	0.24
4	OC_6H_{13}	20 (13)[a]	0.29
5	OC_9H_{19}	27 (26)[a]	0.27
6	$OC_{12}H_{25}$	31	0.33
7	$O{=}COC_4H_9$	23	0.25
8	CN	37 (0)[a]	0.21



Compound no.	X	Y	Range, °C	Optical pitch, μm
9	H	H	${}_{123}\underline{\mathrm{Ch}}_{132}$	0.15
10	Cl	Cl	${}_{98}\underline{\mathrm{S}}\,{}_{103}\underline{\mathrm{Ch}}_{111}$	0.18
11	CH_3	H	${}_{71}\underline{\mathrm{S}}_{93}$	0.17

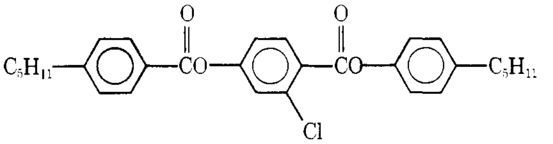


Compound no.	R	X	Y	Range, °C	Optical pitch, μm
12	C_3H_7	H	Cl	${}_{35}\underline{\mathrm{Ch}}_{92}$	0.32
13	C_4H_9	H	Cl	${}_{40}\underline{\mathrm{Ch}}_{86}$	0.32
14	C_5H_{11}	H	Cl	${}_{47}\underline{\mathrm{Ch}}_{95}$	0.32
15	C_5H_{11}	Cl	H	${}_{68}\underline{\mathrm{Ch}}_{102}$	0.37
16	C_6H_{13}	H	Cl	${}_{36}\underline{\mathrm{Ch}}_{80}$	0.32
17	C_8H_{17}	H	Cl	${}_{36}\underline{\mathrm{Ch}}_{83}$	0.34

[a] Monotropic

Typical examples of three types of chiral nematic esters are shown in Table I. The simple esters often exhibit a monotropic mesophase (**4**, **5**, **8**) and the phenylene diesters **9–17** are enantiotropic, wherein the phenylene diesters **12–17** with unsymmetrical ester linkages have the lower and broader ranges. As expected, the simple-ester alkyl derivatives **1** and **2** are lower melting than the alkoxy derivatives **3–6**. The simple-ester cyano derivative **8** is monotropic, but compatible with other mesomorphic esters as a mixture component of high positive dielectric anisotropy. Chiral nematic phenylene diesters with unsymmetrical ester linkages have broad cholesteric ranges extending from just above room temperature. As with the nematic esters of this type[12,14] the position of the lateral chlorine atom has a pronounced effect upon the lower end of the mesomorphic range (compare **14** with **15**). These diesters are obviously well-suited for components in broad range mixtures.

Measurements of the "handedness" of these new cholesteric materials indicate that they possess right-handed cholesteric characteristics, in contrast to the majority of cholesteryl-based materials, which are left-handed. Furthermore, they are very tightly "wound"; that is, they have a small optical pitch which affects ultraviolet radiation. In order to measure the optical pitch of these compounds and avoid the ultraviolet molecular absorption, it is necessary to measure the optical pitch of binary mixtures of a chiral nematic compound with a similar-type optically inactive nematic compound. Ideally, the mixtures should consist of the chiral nematic and its racemate.[15] From a practical point of view, we chose the dipentyl phenylene diester **18**



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because of its structural similarity to the chiral nematic esters, especially with respect to the phenylene diesters, as well as its low, broad nematic range (39-122°). Thus, monotropic chiral nematics are rendered "enantiotropic" and high-melting materials are rendered "lower melting." Furthermore, the melting-point-depression effect of mixtures enables many measurements to be made at or near room temperature.

All the optical-pitch values,[16] except for one example, are smaller than any previously reported (0.357 μm);[3] indeed, the symmetrical phenylene diesters display values (0.15-0.18 μm) approximately half that magnitude and which are the smallest known to date. Compound **3** is similar in size to its Schiff-base counterpart[3] but has an optical-pitch value 50% smaller (0.24 vs. 0.357 μm).

Note also that the "tighter" the helix, that is, the lower the optical pitch, the more optically active group(s) as a percent of the molecular size. Thus, the symmetrical phenylene diesters **9-11** with two chiral centers have the smallest optical pitch values and the highest percentage of optical activity, and the simple esters have intermediate values. In addition, the importance of having the chiral alkyl group attached directly to the aromatic system without an intervening oxygen atom or other functionality has been demonstrated and supports our premise that, in general, chiral alkyl (as opposed to alkoxy) groups, and specifically the chiral 2-methylbutyl group, favor chiral nematics with small optical-pitch values. Furthermore, the distance of the chiral center from an aromatic ring, the number of chiral centers, and the size of the molecule are critical factors affecting the magnitude of the optical-pitch value. Since these new chiral nematic esters are right-handed cholesterics, encompass a broad spectrum of temperature ranges, are based on the relatively stable ester linkage, and have very small optical-pitch characteristics such that they can be "diluted" to become color active, these materials offer more stable useful alternatives to and complement the well-known cholesteric liquid crystals based on the cholesteryl moiety.

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(15) Separate measurements employing chiral nematic unsymmetrical phenylene diesters **13** and **14** and their respective racemates led to the same optical-pitch values as obtained using **18** instead of the racemates. Similarly, the use of a nematic simple ester, 4′-hexyloxyphenyl *4-pentylbenzoate, with chiral nematic simple ester* **4**, *having the same* molecular weight, gave values identical with those obtained with **18**, a somewhat longer molecule.
(16) The optical-pitch measurements were made at 28° using a Cary Model 14 spectrometer to scan transmitted light of Grandjean films of mixtures of chiral nematics and **18** absorbing between 350 and 1600 nm. The inverse optical pitch, $1/\lambda$, is plotted against the weight percent chiral nematic in the mixture. Extrapolation to 100% chiral nematic gives the inverse optical pitch for the pure chiral nematic compound. The optical-pitch values (λ or $\bar{n}p$) are given in Table I.

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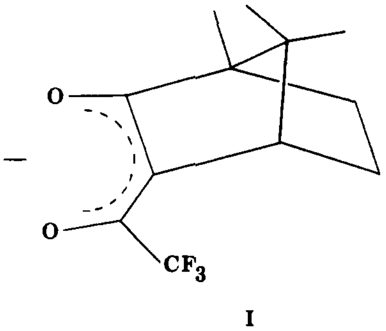
The Structure of an Adduct of a Chiral Lanthanide Nuclear Magnetic Resonance Shift Reagent

Sir:

Complexes between trivalent lanthanide ions and optically active β-diketones have been used to facilitate the determination of enantiomeric purity by NMR methods.[1] Chiral lanthanide complexes were first reported to be useful probes by Whitesides and Lewis.[2] In addition to the well-known lanthanide induced isotropic shifts, the presence of asymmetric centers in the β-diketonato ligands produces a differential shift between the resonances of equivalent nuclei in an enantiomeric pair. Although other optically active β-diketones have been investigated as potential ligands,[3] the most widely used chiral shift reagents are based on 3-trifluoroacetyl-*d*-camphor[4,5] (I).

Despite the wide interest in and use of these reagents, no determination of the structure of a chiral lanthanide shift reagent has previously been reported and little is known about the detailed bonding and steric requirements of these complexes. Without such information chiral shift reagent



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