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(54) Title of Invention: Optically Active Pantolactone Derivatives

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SPECIFICATION

1. Title of Invention
   Optically Active Pantolactone Derivatives

2. Claim
   Optically active pantolactone derivatives shown by general formula (1)

   \[
   R-X-(A_1-Y)-A_2-Z
   \]

   (wherein R indicates a \( C_1-C_{18} \) straight-chain alkyl group, \( C_2-C_{18} \) optically active monohalogenated alkyl group, methyl-branch alkyl group with a \( C_3-C_{18} \) straight-chain section, methyl-branch alkyl ether group or methyl-branch alkyl thioether group containing a total of 4-18 carbon and oxygen or sulfur atoms in the straight-chain section;

   \( X \) indicates \(-\text{co-}, -\text{o-}, -\text{oU-}, \text{or single bond};\)

   \( Y \) indicates \(-\text{co-}, -\text{o-}, -\text{OCH}_2-, -\text{CH}_2\text{O-}, \text{or single bond};\)

   \( Z \) indicates \(-\text{co-}, -\text{O-}, \text{or -CH}_2\text{O-};\)

   \( A_1 \) and \( A_2 \) independently indicate

   \[
   \begin{array}{c}
   \text{B} \\
   \text{N} \\
   \text{B} \\
   \text{N} \\
   \text{B} \\
   \text{N} \\
   \text{B} \\
   \text{N} \\
   \text{B} \\
   \text{or} \\
   \text{B'} \\
   \text{N} \\
   \text{B} \\
   \text{N} \\
   \text{B} \\
   \text{N} \\
   \text{B} \\
   \text{N} \\
   \text{B} \\
   \text{or} \\
   \text{B'} \\
   \end{array}
   \]

   [where \( B \) and \( B' \) independently indicate hydrogen atoms, halogen atoms, or cyano groups];

   \( m \) is 0 or 1;

   and * indicates an asymmetric carbon).

3. Detailed Description of the Invention
   Field of use of the invention
   The present invention relates to novel liquid crystal compounds.

   Prior art
   The liquid crystals widely used as a display material at present belong to the nematic
phase, and although they are the light-receiving type and therefore characterized by not causing eye fatigue and by very low power consumption, they have the drawbacks of slow response and that the display cannot be seen from some viewing angles.

Display devices and printer heads using ferroelectric liquid crystals as having the characteristics of nematic liquid crystals, namely, not causing eye fatigue and consuming very little power, and also having high-speed response and high contrast that rival light-emitting display elements have been investigated.

The existence of ferroelectric liquid crystals was first publicized by R. B. Meyer et al. in 1975 (J. Physique 36, L-69 (1975)). These have a chiral smectic C phase (hereinafter abbreviated Sm*C phase). A typical example of that is p-decyloxybenzylidene-p’-amino-2-methylbutyl cinnamate (hereinafter abbreviated DOBAMBC).

Problems the invention is to solve

However, this DOBAMBC and many of the ferroelectric liquid crystal materials proposed thereafter exhibit ferroelectric properties in a narrow temperature range (the temperature range in which the Sm*C phase is present), and it is difficult to put them to practical use by themselves. Consequently, attempts have usually been made to expand the temperature range that exhibits the Sm*C phase on the lower and higher sides of room temperature by mixing several kinds ferroelectric liquid crystals. Also, for printer head use, which demands ultra-high speed response, ferroelectric liquid crystals with still greater spontaneous polarization than the ferroelectric liquid crystals developed in the past are sought. Further, compounds with Schiff bases such as DOBAMBC were deficient in stability to light and colored easily.

The objective of this invention is to provide optically active compounds that are useful as ferroelectric liquid crystals or as compounding ingredients for these that are chemically stable and do not color and are also outstanding in light stability and exhibit a high response speed.

Means of solving the problems

That is, the gist of this invention is optically active pantolactone derivatives shown by general formula (1).
R-X-(A₁-Y)-A₂-Z

(1)

(wherein R indicates a C₁-C₁₈ straight-chain alkyl group, C₂-C₁₈ optically active monohalogenated alkyl group, methyl-branch alkyl group with a C₃-C₁₈ straight-chain section, methyl-branch alkyl ether group or methyl-branch alkyl thioether group containing a total of 4-18 carbon and oxygen or sulfur atoms in the straight-chain section;

X indicates \(-\text{co-}, \text{-oc-}, \text{-O-}, \text{or single bond;}\)

Y indicates \(-\text{co-}, \text{-oc-}, \text{-OCH}_2-, \text{-CH}_2\text{O-}, \text{or single bond;}\)

Z indicates \(-\text{co-}, \text{-O-}, \text{or -CH}_2\text{O-};\)

A₁ and A₂ independently indicate

\[
\begin{array}{cccc}
B & B & B & B \\
\text{or} & \text{or} & \text{or} & \text{or} \\
N & N & N & N \\
\end{array}
\]

[where B and B' independently indicate hydrogen atoms, halogen atoms, or cyano groups];

m is 0 or 1;

and * indicates an asymmetric carbon).

In the case of the optically active pantolactone derivatives of this invention, when R in general formula (1) is a straight-chain alkyl group, the alkyl group contains 1-18 carbons. But from the standpoint of compatibility with other liquid crystals, it preferably contains 4-14 carbons. As examples of such straight-chain alkyl groups, the n-butyl, n-pentyl, n-hexyl, n-octyl, n-nonyl, n-decyl, n-dodecyl, and n-tetradecyl groups can be mentioned. When R is an optically active methyl-branch alkyl group, the straight-chain section of the alkyl group contains 3-18 carbons. But from the standpoint of compatibility with other liquid crystals, it preferably contains 4-14 carbon atoms. As an example of such optically active methyl-branch alkyl groups, methyl-branch alkyl groups such as

\[
\begin{array}{cccc}
\text{CH}_3 & \text{-(CH}_2)_a \text{CH}_3 \text{-(CH}_2)_b \text{CH}_3 \\
\end{array}
\]

(a indicates an integer of 0 to 11, and b indicates an integer of 1-12; and 1 \leq a + b \leq 12).
When R is an optically active monohalogenated alkyl group, the alkyl group contains 2-18 carbon atoms. But from the standpoint of compatibility with other liquid crystals, it preferably contains 4-14 carbon atoms. As the preferred examples of such optically active monohalogenated alkyl groups, the compounds shown by

\[-(\text{CH}_2)_k \text{CH}(\text{CH}_2)_i \text{CH}_3\]

(where W indicates fluorine, chlorine, or bromine, and k and i are both integers of 0-12; and 
\[2 \leq k + i \leq 12\]) can be mentioned.

When R is an optically active methyl-branch alkyl ether or optically active methyl-branch alkyl thioether, the total number of carbon atoms and oxygen or sulfur atoms in the straight-chain section is 4-18, but the compounds shown by

\[-(\text{CH}_2)_p \text{CH}(\text{CH}_2)_q B(\text{CH}_2)_r \text{CH}_3\]

(where B is -O- or -S-, and p, q, and r are all integers of 0-12; and 
\[1 \leq p + q + r \leq 15\]) are preferred. When compatibility with other liquid crystals is considered, \(p + q + r\) is preferably 
\[\leq p + q + r \leq 11\].

Methods for producing the optically active pantolactone derivatives of this invention will now be explained.

The pantolactone derivatives shown by general formula (1) can be synthesized by the routes shown below.

The routes shown below can be used when \(A_1\) and \(A_2\) have any of the structures indicated earlier.

a) When \(m = 0\) and both \(X\) and \(Z\) are \(-\text{CO}-\) :
b) When \( m = 0 \), \( X = -\text{CO} - \), and \( Z = -\text{O} - \):

\[
\text{AcO-As-CH}_3\text{OH} + \begin{array}{c}
\text{H}_2\text{C} \\
\text{CH}_3
\end{array} \rightarrow \begin{array}{c}
\text{AcO-As-CH}_3\text{O} \\
\text{CH}_3
\end{array}
\]

\[
\begin{array}{c}
\text{PPh}_3, (\text{NOCOCH}_3)_2 \\
\rightarrow
\end{array} \begin{array}{c}
\text{AcO-As-CO} \\
\text{H}_2\text{C} \\
\text{CH}_3
\end{array}
\]

\[
\begin{array}{c}
\text{LiOH} \\
\rightarrow
\end{array} \begin{array}{c}
\text{HO-As-CO} \\
\text{H}_2\text{C} \\
\text{CH}_3
\end{array}
\]

\[
\begin{array}{c}
\text{RCOCl, pyridine} \\
\rightarrow
\end{array} \begin{array}{c}
\text{R-CO-As-CO} \\
\text{H}_2\text{C} \\
\text{CH}_3
\end{array}
\]

c) When \( m = 0 \), \( X = -\text{CO} - \), and \( Z = -\text{CH}_2\text{O} - \):

\[
\text{AcO-As-CH}_3\text{OH} \xrightarrow{\text{CBr}_3, \text{PPh}_3} \text{AcO-As-CH}_3\text{Br}
\]

\[
\text{AcO-As-CH}_3\text{Br} + \begin{array}{c}
\text{H}_2\text{C} \\
\text{CH}_3
\end{array} \rightarrow \begin{array}{c}
\text{AcO-As-CH}_3\text{O} \\
\text{CH}_3
\end{array}
\]
d) When \( m = 0, \ X = -O-, \) and \( Z = -\text{CO}^-:\)

\[
\begin{align*}
\text{HO-A}_2\text{-COH} & \xrightarrow{\text{RBr, K}_2\text{CO}_3} \text{RO-A}_2\text{-COH} \\
\text{RO-A}_2\text{-COH} + \text{HO-A}_2\text{-COH} & \xrightarrow{\text{PPh}_3, (\text{NCO})_2\text{CaH}_2} \text{RO-A}_2\text{-COH}
\end{align*}
\]
e) When $m = 0$, and both $X$ and $Y$ are $\text{-O-}$:

\[
\begin{align*}
\text{HO-Ar-0} & \xrightarrow{\text{RBr, NaH}} \text{RO-Ar-0} \\
\end{align*}
\]

f) When $m = 0$, $X = \text{-O-}$, and $Z = \text{-CH}_2\text{O-}$:

\[
\begin{align*}
\text{HO-Ar-CH}_2\text{O} & \xrightarrow{\text{RBr, NaH}} \text{RO-Ar-CH}_2\text{O} \\
\end{align*}
\]

g) When $m = 0$, $X = \text{-OC-}$, and $Z = \text{-CO-}$:

\[
\begin{align*}
\text{HO-C-Ar-COH} + 2\text{C}_{6}\text{H}_5\text{Br} & \xrightarrow{\text{K}_2\text{CO}_3} \text{C}_{6}\text{H}_5\text{OC-Ar-COH} \\
\text{KOH} & \xrightarrow{} \text{C}_{6}\text{H}_5\text{OC-Ar-COH} \\
\text{C}_{6}\text{H}_5\text{OC-Ar-COH} & + \text{C}_{6}\text{H}_5\text{OH} \\
\text{PPh}_3\cdot (\text{NC}_{6}\text{H}_5\text{CO})_2 & \xrightarrow{} \text{C}_{6}\text{H}_5\text{OC-Ar-CO-} \\
\text{H}_2, \text{Pd}/\text{C} & \xrightarrow{} \text{HO-C-Ar-CO-} \\
\text{ROH, DCC} & \xrightarrow{} \text{RO-C-Ar-CO-} \\
\end{align*}
\]
h) When \( m = 0, X = -\text{O}^-, \) and \( Z = -\text{O}^-: \)

\[
\text{HOC-A} - \text{OAc} \xrightarrow{\text{ROH, DCC}} \text{ROC-A} - \text{OAc}
\]
\[
\text{LiOH} \xrightarrow{} \text{ROC-A} - \text{OH}
\]
\[
\text{ROC-A} - \text{OH} + \text{H}_2\text{C-CH}_3 \xrightarrow{} \text{HOC-A} - \text{OAc}
\]

\[
\text{PPh}_3, (\text{NOCl}_3\text{C}_6\text{H}_5)_n \xrightarrow{} \text{ROC-A} - \text{OAc}
\]

i) When \( m = 0, X = -\text{O}^-, \) and \( Z = -\text{CH}_2\text{O}^-: \)

\[
\text{CH}_3\text{OC-A} - \text{COH} \xrightarrow{\text{BuOH}}
\]
\[
\text{CH}_3\text{OC-A} - \text{CH}_2\text{OH} \xrightarrow{\text{CH}_3\text{c}, \text{PPh}_3}
\]
\[
\text{CH}_3\text{OC-A} - \text{CH}_2\text{Br} \xrightarrow{\text{Ag}_2\text{O}}
\]
\[
\text{CH}_3\text{OC-A} - \text{CH}_2\text{Br} + \text{HOC-A} - \text{CH}_2\text{O} \xrightarrow{\text{H}_2, \text{Pd/C}}
\]
\[
\text{ROH, DCC} \xrightarrow{} \text{HOC-A} - \text{CH}_2\text{O}
\]

j) When \( m = 0, X \) is a single bond, and \( Z = -\text{CO}^-: \)

\[
\text{R-A} - \text{COH} + \text{HOC-A} - \text{HOH} \xrightarrow{\text{PPh}_3, (\text{NOCl}_3\text{C}_6\text{H}_5)_n}
\]
\[
\text{R-A} - \text{CO-}
\]
k) When \( m = 0 \), \( X \) is a single bond, and \( Z = -O- \):

\[
\begin{align*}
\text{HO-C-Ar-OCH}_3 & \xrightarrow{\text{SOCl}_2} \text{C\&C-Ar-OCH}_3 \\
\text{R'-MeBr} & \xrightarrow{\text{R'}-C-Ar-OCH}_3 \xrightarrow{\text{hydroxide}} \text{R-Ar-OCH}_3 \\
\text{R-Ar-OH} & \xrightarrow{\text{PPh}_3, (\text{NO})_2\text{Cu}} \text{R-Ar-O(CH}_3
\end{align*}
\]

l) When \( m = 0 \), \( X \) is a single bond, and \( Z = -\text{CH}_2O- \):

\[
\begin{align*}
\text{R-Ar-CH}_3\text{COH} & \xrightarrow{\text{BuLi}} \text{R-Ar-CH}_3\text{OH} \\
\text{CBr}_3, \text{PPh}_3 & \xrightarrow{} \text{R-Ar-CH}_3\text{Br} \\
\text{R-Ar-CH}_3\text{Br} & \xrightarrow{\text{Ag}_2\text{O}} \text{R-Ar-CH}_3\text{O}\text{(R'=CH}_3)
\end{align*}
\]

m) When \( m = 1 \), \( Y = -\text{CO-} \), and \( Z = -\text{CO-}, -\text{O-}, \) or \(-\text{CH}_2O-\):

This derivative can be obtained in the same manner as a), b), or c) except for using \( \text{R-X-Ar-COCl} \) instead of \( \text{RCOCl} \).

n) When \( m = 1 \), \( Y = -\text{O-} \), and \( Z = -\text{CO-}, -\text{O-}, \) or \(-\text{CH}_2O-\):

This derivative can be obtained in the same manner as g), h), or i) except for using \( \text{R-X-Ar-OH} \) instead of \( \text{ROH} \).

o) When \( m = 1 \), \( Y = -\text{CH}_2O- \), and \( Z = -\text{CO-}, -\text{O-}, \) or \(-\text{CH}_2O-\):

This derivative can be synthesized by the following route using the intermediate

\[
(Z = -\text{CO-}, -\text{O-}, \) or \(-\text{CH}_2O-\) obtained in the course of the reaction of a), b), or c).
p) When \( m = 1, Y = -\text{OCH}_2-, \) and \( Z = -\text{CO}- \) or \(-\text{CH}_2\text{O}-:\)

This derivative can be synthesized by the following route using the intermediate

\[
\text{HO\text{-}C\text{-}A\text{_r}\text{-}Z}\quad \text{H}_3\text{C}\text{\_CH}_2\text{H}_3
\]

\( Z = -\text{CO}- \) or \(-\text{O}- \) obtained in the course of the reaction of g) or h).

q) When \( m = 1, Y = \text{OCH}_2-, \) and \( Z = -\text{O}-:\)

\[
\text{R\text{-}X\text{-}A\text{_r}\text{-}OH} + \text{BrCH}_2\text{-A\text{_r}\text{-}Z}
\]

\[
\text{R\text{-}X\text{-}A\text{_r}\text{-}OCH}_3\text{-A\text{_r}\text{-}Z}
\]

\[
\text{R\text{-}X\text{-}A\text{_r}\text{-}OCH}_3\text{-A\text{_r}\text{-}OAc}
\]

\[
\text{R\text{-}X\text{-}A\text{_r}\text{-}OCH}_3\text{-A\text{_r}\text{-}OH}
\]
Among the compounds of this invention, those where B and B' in general formula (1) are halogen atoms or cyano groups are characterized by a broad temperature range showing the Sm* C phase and also a lower boiling point than the corresponding compounds that do not have a halogen atom or cyano group.

Among the optically active pantolactone derivatives of this invention are some that show a liquid crystal phase and some that do not show a liquid phase by themselves, but even those that do not show a liquid crystal phase by themselves have the property of inducing a ferroelectric phase (Sm*C phase) by adding 1-90 mol% in a range that does not destroy the liquid crystal property to non-chiral liquid crystals or liquid crystal compositions that show a phase system of isophase-nematic phase-smectic A phase-smectic C phase (SmC phase) or isophase-nematic phase-SmC phase.

Therefore, even those that do not show a liquid crystal phase by themselves can be used as ideal compounding agents when preparing ferroelectric liquid crystal compositions.

Also, the optically active pantolactone derivatives of this invention are characterized by outstanding chemical stability such as hydrolysis resistance because they do not contain the azomethine linkages often found in conventional ferroelectric liquid crystal compounds and, along with that, outstanding light stability because they do not have vinyl groups such as seen in the liquid crystals of cinnamic acid systems.

Also, the optically active pantolactone derivatives of this invention that show ferroelectric liquid crystal properties by themselves can be used as liquid crystals alone, but if they are used in compositions with a plural number of ferroelectric liquid crystal compounds or with compounding ingredients added to these rather than as liquid crystals formed from only a single liquid crystal compound, the usable temperature range can be expanded, so they become more advantageous.

Also, when the optically active pantolactone derivatives of this invention are used mixed with non-ferroelectric liquid crystal compounds or compositions that show the SmC phase, that mixture becomes ferroelectric liquid crystals and, moreover, exhibits great spontaneous polarization, as is clear from the high response speed, and is useful.

As the above-mentioned compounds that are mixed with the optically active pantolactone derivatives, any compounds or mixtures can be used as long as they show the SmC phase.
Practical examples

This invention will now be explained in further detail using practical examples, but it is not limited to these practical examples.

Practical Example 1

Synthesis of (2R)-4'-decyloxybiphenyl-4-carbonyloxy-3,3-dimethyl-γ-butyrolactone

0.34 g of 4'-decyloxy-4-biphenylcarboxylic acid, 0.16 g of D-(−)-pantoyllactone (sold by Tokyo Kasei), and 0.21 g of diethyl azodicarboxylate were dissolved in 10 mL of benzene, and 0.30 g of triphenylphosphine was added. This was continuously stirred and reacted overnight at room temperature. The solvent was distilled off from the reaction solution obtained to get a crude product, and this was purified by silica gel column chromatography to obtain 0.15 g of (2R)-4'-decyloxybiphenyl-4-carbonyloxy-3,3-dimethyl-γ-butyrolactone. This was also recrystallized using ethanol, and 0.10 g of pure product was obtained. The phase transition behavior of this compound was determined using a differential scanning calorimeter and a polarizing microscope. The results are shown below.

In the phase transition behavior, Cryst. indicates crystalline, and the numbers near the arrows indicate the transition temperature (°C) to that phase.

Practical Example 2

A liquid crystal composition was obtained by mixing the four alkoxyphenylpyrimidine compounds shown below.

```
C₆H₄O-\begin{array}{c}
| N |
\end{array}OC₆H₄ \quad 24\text{mol}\%
```

```
C₆H₁₄O-\begin{array}{c}
| N |
\end{array}OC₆H₄ \quad 36\text{mol}\%
```

```
C₆H₁₄O-\begin{array}{c}
| N |
\end{array}OC₆H₄ \quad 24\text{mol}\%
```

```
C₁₁H₂₆O-\begin{array}{c}
| N |
\end{array}OC₆H₄ \quad 16\text{mol}\%
```

This composition shows the following phase transition behavior.

```
Cryst \quad \text{SmC} \quad \text{SmA} \quad \text{N} \quad \text{Isa}
```

This composition does not contain an optically active compound, so it is not ferroelectric.
liquid crystals and does not show spontaneous polarization.

A ferroelectric liquid crystal composition was obtained by mixing 98 wt% of this compound with 2 wt% of (2R)-4'-decyloxybiphenyl-4-carboxyloxy-3,3-dimethyl-γ-butyrolactone.

The phase transition behavior of this composition was as follows.

\[
\text{Cryst} \xrightarrow[24]{2.4} \text{Sm}\cdot\text{C} \xrightarrow[49]{60} \text{SmA} \xrightarrow[64]{64} \text{N}^* \xrightarrow[70]{64} \text{Iso}
\]

A liquid crystal element was produced by pouring this ferroelectric liquid composition in a cell 2 μm deep equipped with transparent electrodes which had been coated with polyimide as polarizing agent and given a parallel orientation treatment by surface rubbing.

This element was placed between two crossed polarizers, and an electric field was applied at 25°C. A change in transmitted light was found by application of ±5V/μm, and the 0-50% response time found from that change was 160 μsec. The magnitude of the spontaneous polarization at 25°C as determined by the triangular wave method was -1.8 nC/cm².

**Effects of the invention**

The optically active pantolactone derivatives of this invention are compounds that are useful as liquid crystal components or as compounding ingredients of ferroelectric liquid crystals that are chemically stable, as is clear from their chemical structure, and do not color, are outstanding in light stability, and also, as indicated above, exhibit great spontaneous polarization and are outstanding in response properties.

Applicant: Mitsubishi Rayon Co., Ltd.