

AUSTRALIA

Patents Act 1990

PATENT REQUEST : STANDARD PATENT

I/We, being the person/s identified below as the Applicant, request the grant of a patent to the person/s indicated below as the Nominated Person/s, for an invention described in the accompanying standard complete specification.

Full application details follow.

[71] [70] Applicant/s and Nominated Person/s:
Hoechst Aktiengesellschaft,
of D-65926 FRANKFURT AM MAIN, GERMANY

[54] Invention Title:
Biquaternary ammonium compounds of 2,2'-dimethyl-1,1'-binaphthyl and
process for their preparation

[72] Name/s of actual inventor/s: (optional)

[74] Address for service in Australia:
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BASIC CONVENTION APPLICATION/S DETAILS:

[31] Appln No.:
P 44 18 349.6

[33] Country:
GERMANY

Code:
DE

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26 May 1994

DATED this EIGHTEENTH day of MAY 1995

Hoechst Aktiengesellschaft
By Patent Attorneys
DAVIES COLLISON CAVE

Peter Stearne

Dr. PETER STEARNE, FIPAA

Fee: \$ 280.00

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A U S T R A L I A

P'00'001 : Section 29

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NOTICE OF ENTITLEMENT

We, Hoechst Aktiengesellschaft, of D-65926 Frankfurt Am Main, Germany, the Applicant in respect of Application No. 20169/95 state the following:

1. Hoechst Aktiengesellschaft is the Nominated Person in respect of the application.
2. The actual inventor of the invention, the subject of the application, is:
Dr. Hans Millauer
3. The Nominated Person, Hoechst Aktiengesellschaft, is entitled to the grant of a patent in respect of the application because the said Nominated Person derived title to the invention from the actual inventor by way of employment contract.
4. The Nominated Person is entitled to claim priority from the basic application listed on the patent request form because (i) the Nominated Person is the Applicant in respect of the basic application; and (ii) the basic application was the first application made in a Convention country in respect of the invention the subject of the application.

Dated this 16th day of September, 1997.

By Its Patent Attorneys
DAVIES COLLISON CAVE


MARK ROBERTS

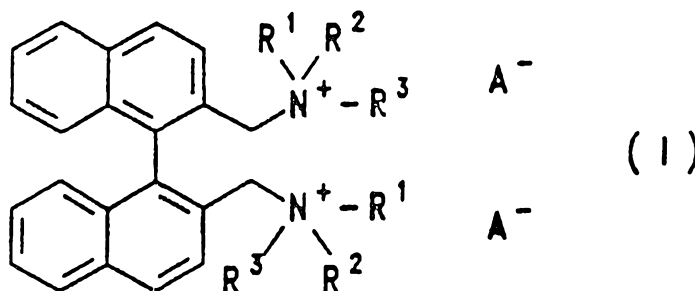


AU9520169

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(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 684921

- (54) Title
BISQUATERNARY AMMONIUM COMPOUNDS OF 2,2'-DIMETHYL-1,1'-BINAPHTHYL AND
PROCESS FOR THEIR PREPARATION
- (51)⁶ International Patent Classification(s)
C07C 211/63 C07C 209/12 C07D 519/00
- (21) Application No. : 20169/95 (22) Application Date : 19.05.95
- (30) Priority Data
- (31) Number (32) Date (33) Country
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- (43) Publication Date : 07.12.95
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- (71) Applicant(s)
HOECHST AKTIENGESELLSCHAFT
- (72) Inventor(s)
DR. HANS MILLAUER
- (74) Attorney or Agent
DAVIES COLLISON CAVE, GPO Box 3876, SYDNEY NSW 2001
- (57) Claim

1. A bisquaternary ammonium compound of the formula (I)



where:

R^1 , R^2 , R^3 are identical or different and are (C_1 - C_{12})alkyl which can also contain oxygen atoms or $N-R^4$ moieties, where R^4 is (C_1 - C_4)alkyl, in the chain or

R^1 is (C_4 - C_8)cycloalkyl and R^2 , R^3 are identical or different and are (C_1 - C_{12})alkyl or

the two radicals R^1 together form an alkylene chain having from 2 to 6 carbon atoms and R^2 , R^3 are identical or different and are (C_1 - C_{12})alkyl or

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(10) 684921

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the radicals R^1 and R^2 located on the same nitrogen atom together form a 5-membered or 6-membered ring, which can also contain oxygen atoms or $N-R^4$ moieties, where R^4 is (C_1-C_4) alkyl, in the chain and the radical R^3 is an alkyl radical having from 1 to 12 carbon atoms or

the radicals R^1 , R^2 , R^3 located on the same nitrogen atom together form a bicyclic ring system having a nitrogen atom as bridge head atom and, if desired, further oxygen atoms or $N-R^4$ moieties, where R^4 is (C_1-C_4) alkyl, in the ring system and

A is a chlorine, bromine, iodine atom or a OSO_3R^5 radical, where R^5 is (C_1-C_4) alkyl or aryl.

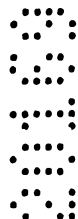
Our Ref: 548922

P/00/011
Regulation 3:2

AUSTRALIA

Patents Act 1990

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT



Applicant(s):

Hoechst Aktiengesellschaft

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Invention Title:

Bisquaternary ammonium compounds of
2,2'-dimethyl-1,1'-binaphthyl and process for their preparation

The following statement is a full description of this invention, including the best method of performing it known to me:-

Description

Bisquaternary ammonium compounds of 2,2'-dimethyl-1,1'-binaphthyl and process for their preparation

5 The invention relates to bisquaternary ammonium compounds of 2,2'-dimethyl-1,1'-binaphthyl and processes for their preparation.

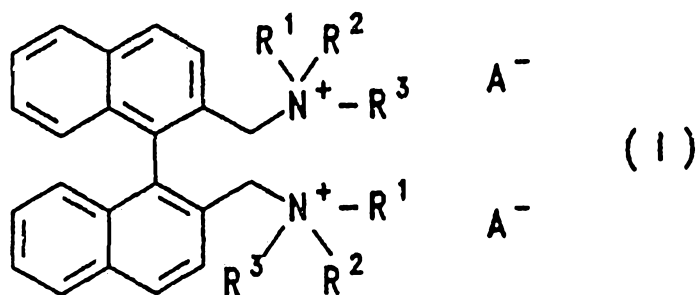
Bisquaternary ammonium compounds of 2,2'-dimethyl-1,1'-binaphthyl are important intermediates for the preparation of bistertiary phosphines.

10 Phosphines having two tertiary phosphine groups in the molecule, which groups bear bulky aromatic or araliphatic radicals, are used as bidentate ligands for complexing heavy metal atoms such as palladium or rhodium. In particular, bidentate ligands which are structurally
15 derived from 1,1'-binaphthyl and bear (diphenylphosphino)methyl groups as substituents in the 2 and 2' positions, known under the term "Naphos", form very stable complexes which are used as catalysts in a series of important industrial processes, e.g. hydrogenations
20 and oxo syntheses.

The German Patent Application P 44 18 346.1, filed on the same day, describes a very advantageous process for preparing tertiary phosphines for which the ammonium compounds of the invention are required as starting
25 materials.

It is thus an object of the invention to provide such compounds.

This object is achieved by compounds of the formula (I)



where:

R^1 , R^2 , R^3 are identical or different and are (C_1-C_{12}) -alkyl which can also contain oxygen atoms or $N-R^4$ moieties, where R^4 is (C_1-C_4) alkyl, in the chain or

- 5 R^1 is (C_4-C_8) cycloalkyl and R^2 , R^3 are identical or different and are (C_1-C_{12}) alkyl or

the two radicals R^1 together form an alkylene chain having from 2 to 6 carbon atoms and R^2 , R^3 are identical or different and are (C_1-C_{12}) alkyl or

- 10 the radicals R^1 and R^2 located on the same nitrogen atom together form a 5-membered or 6-membered ring, which can also contain oxygen atoms or $N-R^4$ moieties, where R^4 is (C_1-C_4) alkyl, in the chain and the radical R^3 is an alkyl radical having from 1 to 12 carbon atoms or

- 15 the radicals R^1 , R^2 , R^3 located on the same nitrogen atom together form a bicyclic ring system having a nitrogen atom as bridge head atom and, if desired, further oxygen atoms or $N-R^4$ moieties, where R^4 is (C_1-C_4) alkyl, in the ring system and

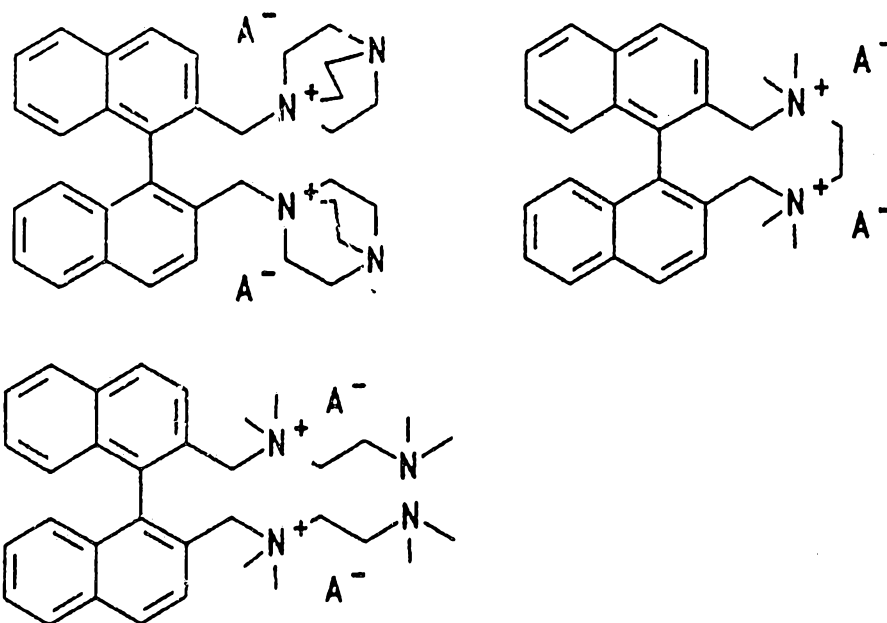
- 20 A is a chlorine, bromine, iodine atom or a OSO_3R^5 radical, where R^5 is (C_1-C_4) alkyl or aryl.

Of great interest are, for example, the following compounds of the formula (I):

2,2'-bis[(trimethylammonio)methyl]-1,1'-binaphthyl salts

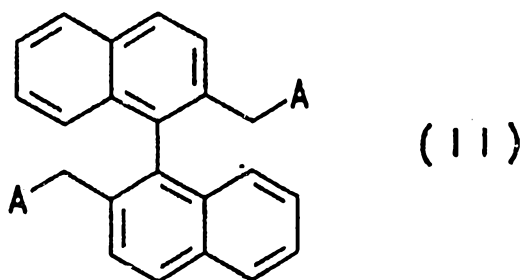
- 2,2'-bis[(triethylammonio)methyl]-1,1'-binaphthyl salts
 2,2'-bis[(tripropylammonio)methyl]-1,1'-binaphthyl salts
 2,2'-bis[(tributylammonio)methyl]-1,1'-binaphthyl salts
 2,2'-bis[(triethylammonio)methyl]-1,1'-binaphthyl salts
 5 2,2'-bis[(trioctylammonio)methyl]-1,1'-binaphthyl salts
 2,2'-bis[(N-ethyltrimethylammonio)methyl]-1,1'-binaphthyl salts
 2,2'-bis[(N,N-dimethylbutylammonio)methyl]-1,1'-binaphthyl salts
 10 2,2'-bis[(N,N-dimethylcyclohexylammonio)methyl]-1,1'-binaphthyl salts
 2,2'-bis[(N,N-dicyclohexylmethylammonio)methyl]-1,1'-binaphthyl salts
 2,2'-bis[(N-methylpiperidinio)methyl]-1,1'-binaphthyl salts
 15 2,2'-bis[(N,N'-dimethylpiperazinio)methyl]-1,1'-binaphthyl salts
 2,2'-bis[(N-methylmorpholinio)methyl]-1,1'-binaphthyl salts.

20 Of particular importance are also:

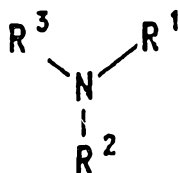


The invention further provides a process for preparing the compounds of the formula (I), which comprises

reacting compounds of the formula (II)



where A is as defined above,
at temperatures of from 20 to 150°C in the presence of a
solvent, at atmospheric or superatmospheric pressure,
5 with a nitrogen base of the formula (III)



where R¹, R² and R³ are as defined above.

Since the products of the invention having the formula
(I) in many cases tend to form stable solvate complexes
with the solvent used, care should be taken in selecting
10 the solvent that this does not interfere in the subse-
quent reaction step. Suitable solvents are, for example,
hydrocarbons, ethers, halogenated hydrocarbons, ketones,
nitro compounds or nitriles.

Solvents which have been found to be suitable in many
15 cases are, for example: isohexane, n-heptane, cyclo-
hexane, hydrocarbon fractions (petroleum spirit) having
boiling point ranges between 70 and 250°C, toluene,
xylene, methyl t-butyl ether, diisopropyl ether, tetra-
hydrofuran, chloroform, chlorobenzene, acetone, methyl
20 i-butyl ketone, nitromethane, acetonitrile, dimethylfor-
mamide and dimethylacetamide; preference is given to
chlorobenzene and dimethylformamide.

The reaction temperatures are preferably from 50 to
120°C. When using readily volatile amines, the use of

increased pressure is useful. The pressure range required is between 1 and about 10 bar. The reaction time is between 1 and 12 hours.

5 The reaction mixture is advantageously stirred continuously during the reaction. The products of the invention having the formula (I) are sparingly soluble in some of the solvents used and precipitate during the reaction. In this case, the products are separated off by filtration. If the process products are soluble, they can be isolated
10 by distilling off the solvent and, if appropriate, the excess amine.

When using certain solvents such as, for example, dimethylformamide, dimethylacetamide, acetonitrile or tetrahydrofuran the isolation of the product can be
15 omitted; in this case the reaction mixture can be used directly in the subsequent reaction step.

The starting compounds of the formula (II) which are required for preparing the products of the invention having the formula (I) can be obtained, for example, by
20 side-chain bromination of 2,2'-dimethyl-1,1'-binaphthyl using known methods. The tertiary amines required as starting compounds of the formula (III) are known and most are commercially available; they are prepared by known methods.

25 Example 1

A stirred flask having a capacity of 100 ml and fitted with a reflux condenser which can be cooled to -20°C, thermometer and heating bath is charged with 11.0 g (0.025 mol) of 2,2'-bis(bromomethyl)-1,1'-binaphthyl,
30 4.43 g (0.075 mol) of trimethylamine in 50 ml of dimethylformamide and the mixture is gradually heated to 70°C while stirring. Stirring is continued for 3 hours at this temperature. After cooling to room temperature, the precipitated product is filtered off with suction, washed
35 with a little cold dimethylformamide and dried in a

vacuum desiccator over concentrated sulfuric acid. The yield is 11.8 g (74% of theory) of 2,2'-bis[(trimethylammonio)methyl]-1,1'-binaphthyl dibromide; after drying, the product still contains one molecule of dimethylformamide.

5

^1H -NMR (300 MHz, D_2O) δ in ppm, D_2O as reference:

7.2 - 8.2 (12 H, aryl-H)

4.7 (2 H, aryl- $\text{CH}^{\text{A}}\text{H}^{\text{B}}\text{-N}^+$)

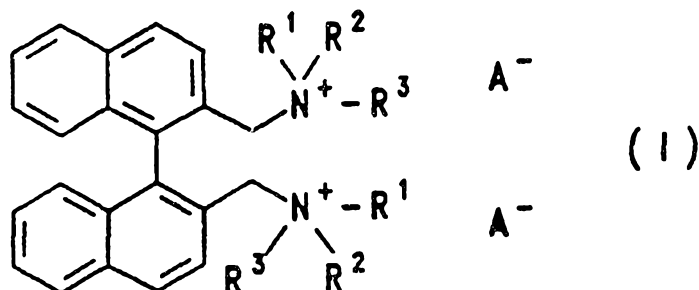
3.9 (2 H, aryl- $\text{CH}^{\text{A}}\text{H}^{\text{B}}\text{-N}^+$, $J_{\text{AB}} = 15 \text{ Hz}$)

10

2.6 (18 H, $\text{-N}^+ (\text{CH}_3)_3$)

The Claims defining the invention are as follows:

1. A bisquaternary ammonium compound of the formula (I)



where:

R^1 , R^2 , R^3 are identical or different and are (C_1 - C_{12})alkyl which can also contain oxygen atoms or $N-R^4$ moieties, where R^4 is (C_1 - C_4)alkyl, in the chain or

R^1 is (C_4 - C_8)cycloalkyl and R^2 , R^3 are identical or different and are (C_1 - C_{12})alkyl or

the two radicals R^1 together form an alkylene chain having from 2 to 6 carbon atoms and R^2 , R^3 are identical or different and are (C_1 - C_{12})alkyl or

the radicals R^1 and R^2 located on the same nitrogen atom together form a 5-membered or 6-membered ring, which can also contain oxygen atoms or $N-R^4$ moieties, where R^4 is (C_1 - C_4)alkyl, in the chain and the radical R^3 is an alkyl radical having from 1 to 12 carbon atoms or

the radicals R^1 , R^2 , R^3 located on the same nitrogen atom together form a bicyclic ring system having a nitrogen atom as bridge head atom and, if desired, further oxygen atoms or $N-R^4$ moieties, where R^4 is (C_1 - C_4)alkyl, in the ring system and

A is a chlorine, bromine, iodine atom or a OSO_3R^5

radical, where R^5 is (C_1-C_4) alkyl or aryl.

2. A compound of the formula (I) from the groups consisting of:

5 2,2'-bis[(trimethylammonio)methyl]-1,1'-binaphthyl salts

2,2'-bis[(triethylammonio)methyl]-1,1'-binaphthyl salts

2,2'-bis[(tripropylammonio)methyl]-1,1'-binaphthyl salts

10 2,2'-bis[(tributylammonio)methyl]-1,1'-binaphthyl salts

2,2'-bis[(trihexylammonio)methyl]-1,1'-binaphthyl salts

15 2,2'-bis[(trioctylammonio)methyl]-1,1'-binaphthyl salts

2,2'-bis[(N-ethyldimethylammonio)methyl]-1,1'-binaphthyl salts

2,2'-bis[(N,N-dimethylbutylammonio)methyl]-1,1'-binaphthyl salts

20 2,2'-bis[(N,N-dimethylcyclohexylammonio)methyl]-1,1'-binaphthyl salts

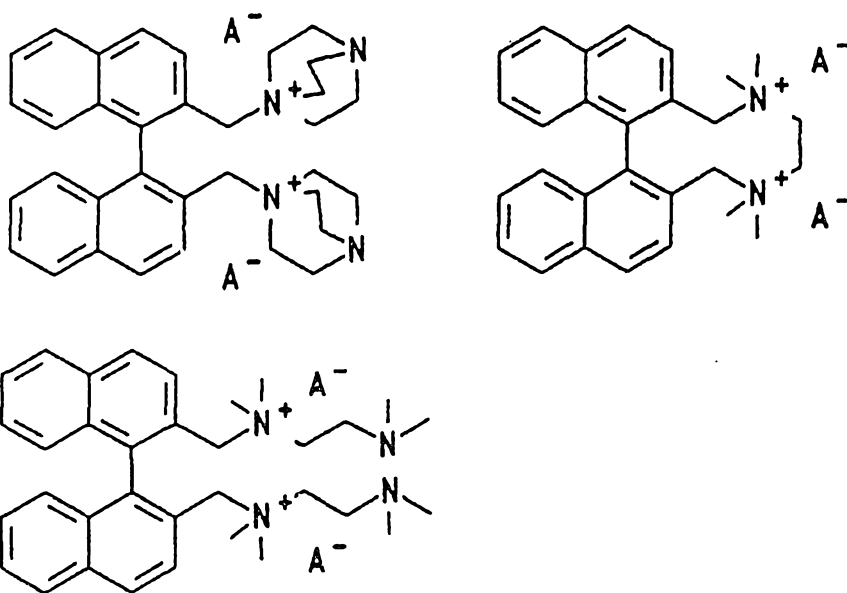
2,2'-bis[(N,N-dicyclohexylmethylammonio)methyl]-1,1'-binaphthyl salts

25 2,2'-bis[(N-methylpiperidinio)methyl]-1,1'-binaphthyl salts

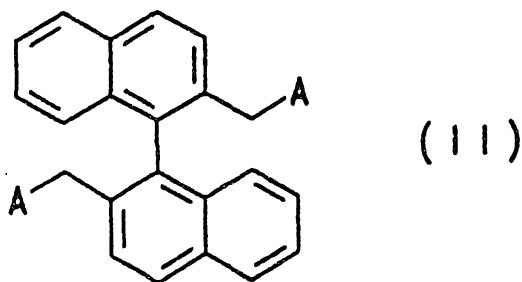
2,2'-bis[(N,N'-dimethylpiperazinio)methyl]-1,1'-binaphthyl salts

2,2'-bis[(N-methylmorpholinio)methyl]-1,1'-binaphthyl salts.

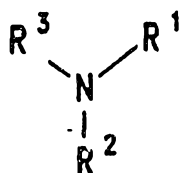
- 30 3. A compound of the formula (I) from the groups consisting of:



4. A process for preparing the compounds of the formula (I), which comprises reacting compounds of the formula (II)



- 5 where A is as defined above,
at temperatures of from 20 to 150°C in the presence
of a solvent, at atmospheric or superatmospheric
pressure,
with a nitrogen base of the formula (III)



where R¹, R² and R³ are as defined above.

5. The process as claimed in claim 4, wherein hydrocarbons, ethers, halogenated hydrocarbons, ketones, nitro compounds or nitriles are used as solvent.
- 5 6. The process as claimed in claim 4, wherein isohexane, n-heptane, cyclohexane, hydrocarbon fractions (petroleum spirit) having boiling point ranges between 70 and 250°C, toluene, xylene, methyl t-butyl ether, diisopropyl ether, tetrahydrofuran, chloroform, chlorobenzene, acetone, methyl i-butyl ketone, nitromethane, acetonitrile, dimethylformamide or dimethylacetamide are used as solvent.
10
7. The process as claimed in claim 4, wherein chlorobenzene or dimethylformamide are used as solvent.
- 15 8. The process as claimed in any one of claims 4 to 7, wherein the reaction is carried out at temperatures of from 50 to 120°C.
9. The process as claimed in any one of claims 4 to 8, wherein the reaction is carried out at a pressure of from 1 to 10 bar.

10. A bisquaternary ammonium compound of the formula (I) according to Claim 1 substantially as hereinbefore described with reference to the examples.
- 5 11. A process for preparing compounds of the formula (I), according to Claim 4 substantially as hereinbefore described with reference to the examples.

DATED this 18th day of May 1995,

HOECHST AKTIENGESELLSCHAFT

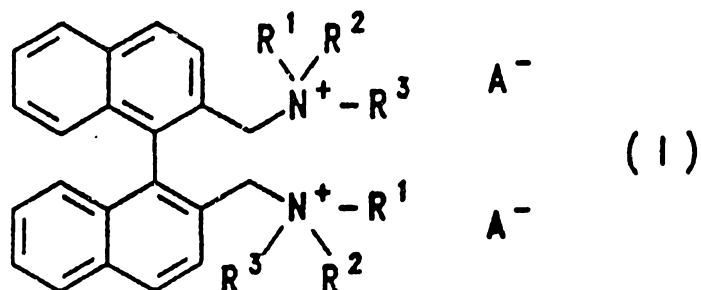
By Its Patent Attorney

DAVIES COLLISON CAVE

10

Abstract

The invention relates to bisquaternary ammonium compounds of the formula (I)



and their preparation, where:

R^1 , R^2 , R^3 are, for example, identical or different (C_1 - C_{12})alkyl which can also contain oxygen atoms or $N-R^4$ moieties, where R^4 is (C_1 - C_4)alkyl, in the chain and A is a chlorine, bromine, iodine atom or a OSO_3R^5 radical, where R^5 is (C_1 - C_4)alkyl or aryl.