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(54) Titre : STABILISATION DE POLYOLEFINES EN CONTACT PERMANENT AVEC LES MILIEUX D'EXTRACTION

(54) Title: STABILIZATION OF POLYOLEFINS IN PERMANENT CONTACT WITH EXTRACTING MEDIA

(57) **Abrégé/Abstract:**

Polyolefin mouldings which have excellent stability on permanent contact with extracting media comprise, as stabilizers, a selected mixture comprising an organic phosphite or phosphonite and a specially selected group of sterically hindered phenols or a certain group of sterically hindered amines. In addition, a selected three-component mixture comprising a phosphite or phosphonite, a phenolic antioxidant and a certain group of sterically hindered amines is particularly suitable as stabilizer for polyolefin mouldings which are in permanent contact with extracting media.

Abstract

Polyolefin mouldings which have excellent stability on permanent contact with extracting media comprise, as stabilizers, a selected mixture comprising an organic phosphite or phosphonite and a specially selected group of sterically hindered phenols or a certain group of sterically hindered amines. In addition, a selected three-component mixture comprising a phosphite or phosphonite, a phenolic antioxidant and a certain group of sterically hindered amines is particularly suitable as stabilizer for polyolefin mouldings which are in permanent contact with extracting media.

Stabilization of polyolefins in permanent contact with extracting media

The present invention relates to compositions comprising a polyolefin which is in permanent contact with extracting media, and stabilizer mixtures, to the use thereof for stabilizing thick-layer polyolefin mouldings, and to a process for stabilizing thick-layer polyolefin mouldings.

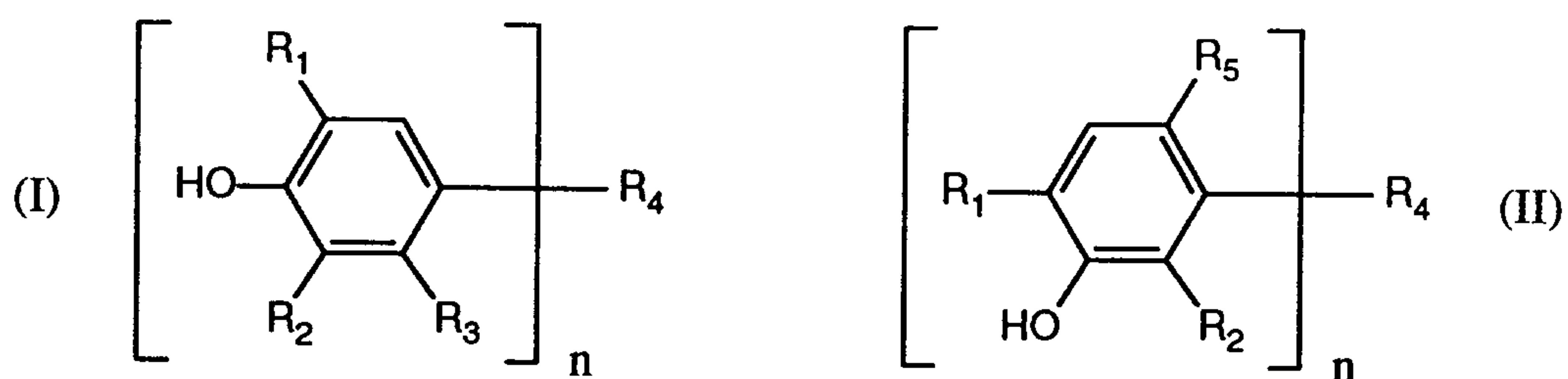
R. Gächter and H. Müller, "Plastics Additives Handbook, 3rd Edition", pages 1 to 100 (1990), discloses, for example, that polyolefins can be protected against oxidative damage during preparation, processing and use by means of suitable stabilizer mixtures. In many cases, the stabilized polyolefin mouldings are in contact with liquid or gaseous media during use. It is therefore necessary that the stabilizer mixtures added to the polyolefin moulding have adequate chemical resistance to the particular contact media. Examples of polyolefin mouldings which are particularly at risk are pipes, undersea cables, tanks and geomembranes which are in permanent contact with extracting media.

EP-A-0 324 106 describes a polyolefin moulding composition which has particularly good stability in permanent contact with extracting media. The stabilizer mixture used is a symmetrical triaryl phosphite and an ester of 3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butanoic acid.

It has now been found that a selected mixture comprising an organic phosphite or phosphonite and a specially selected group of sterically hindered phenols or a certain group of sterically hindered amines are particularly suitable as stabilizers for polyolefin mouldings which are in permanent contact with extracting media. It has also been found that a three-component mixture comprising a phosphite or phosphonite, a phenolic antioxidant and a certain group of sterically hindered amines is particularly suitable as stabilizer for polyolefin mouldings which are in permanent contact with extracting media.

The present invention therefore relates to compositions comprising

- a) a polyolefin which is in permanent contact with extracting media,
- b) at least one compound from the group consisting of organic phosphites or phosphonites,
- c) (i) at least one compound of the formula I or II



in which

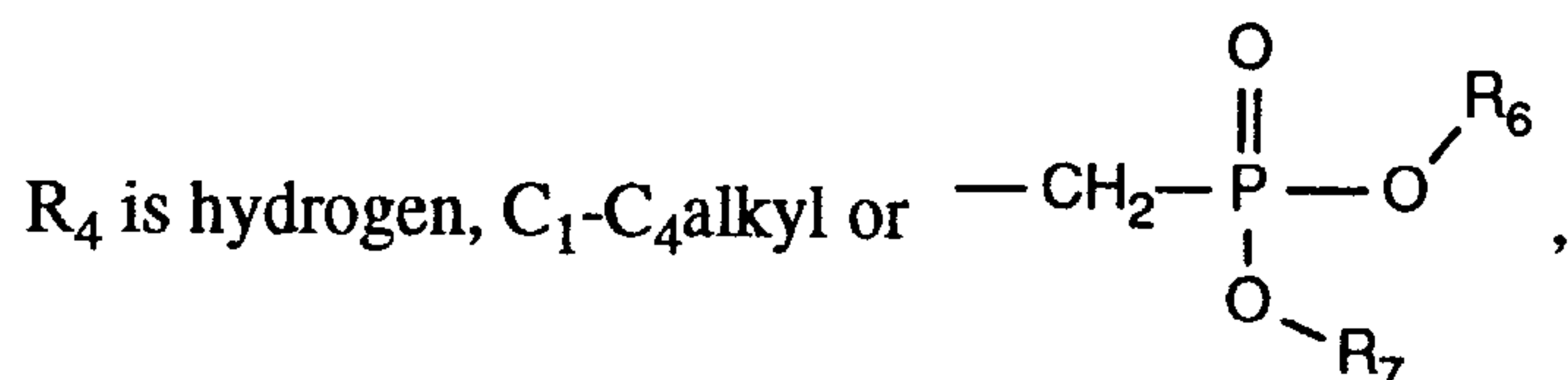
n is the number 1 or 3,

R_1 is C_1 - C_{18} alkyl, C_5 - C_{12} cycloalkyl, phenyl or C_7 - C_9 phenylalkyl,

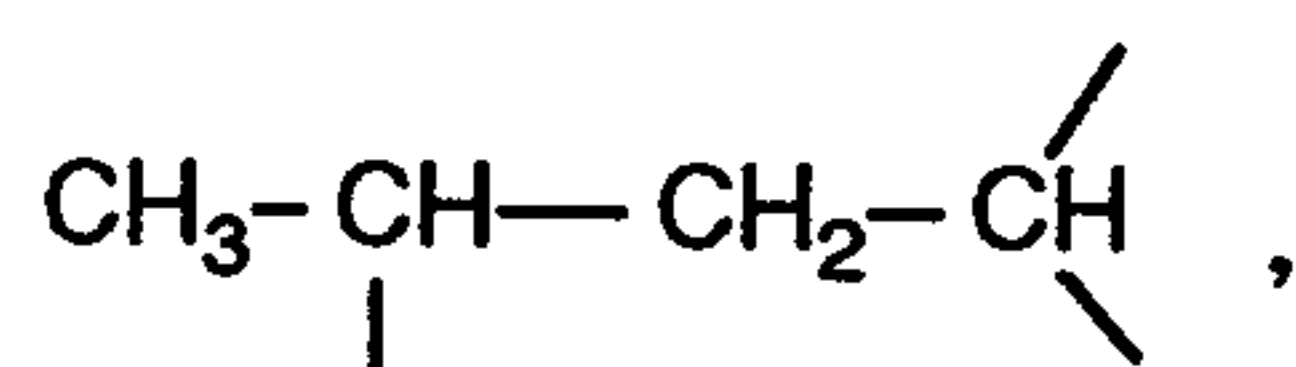
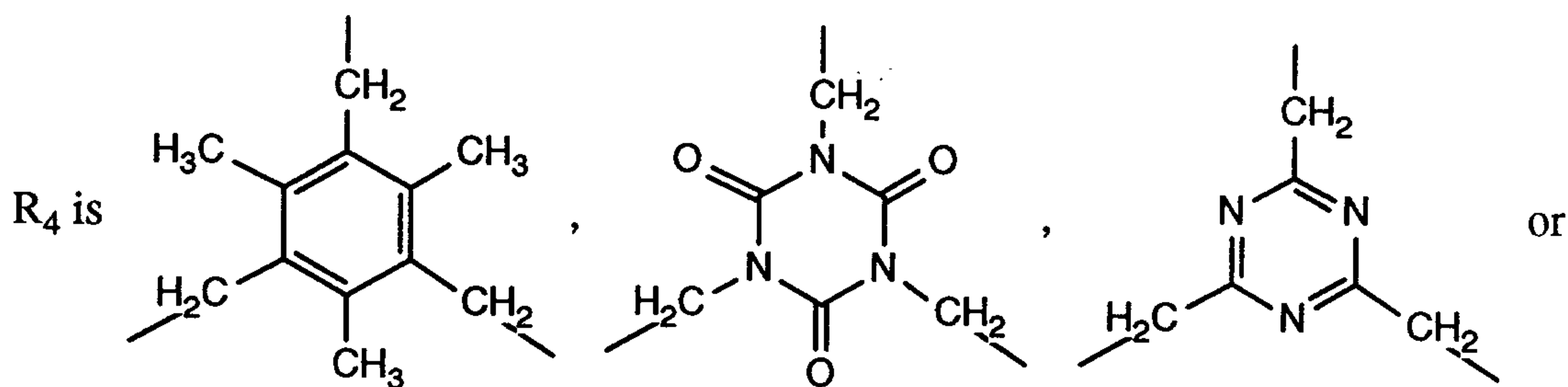
R_2 is hydrogen, C_1 - C_{18} alkyl, C_5 - C_{12} cycloalkyl, phenyl or C_7 - C_9 phenylalkyl,

R_3 is hydrogen or methyl,

if n is 1,



if n is 3,



R_5 is hydrogen or methyl,

R_6 is hydrogen, C_1 - C_{20} alkyl, unsubstituted or C_1 - C_4 alkyl-substituted phenyl or

naphthyl; or $\frac{\text{M}^{r+}}{r}$,

R_7 is C_1 - C_{20} alkyl, unsubstituted or C_1 - C_4 alkyl-substituted phenyl or naphthyl,

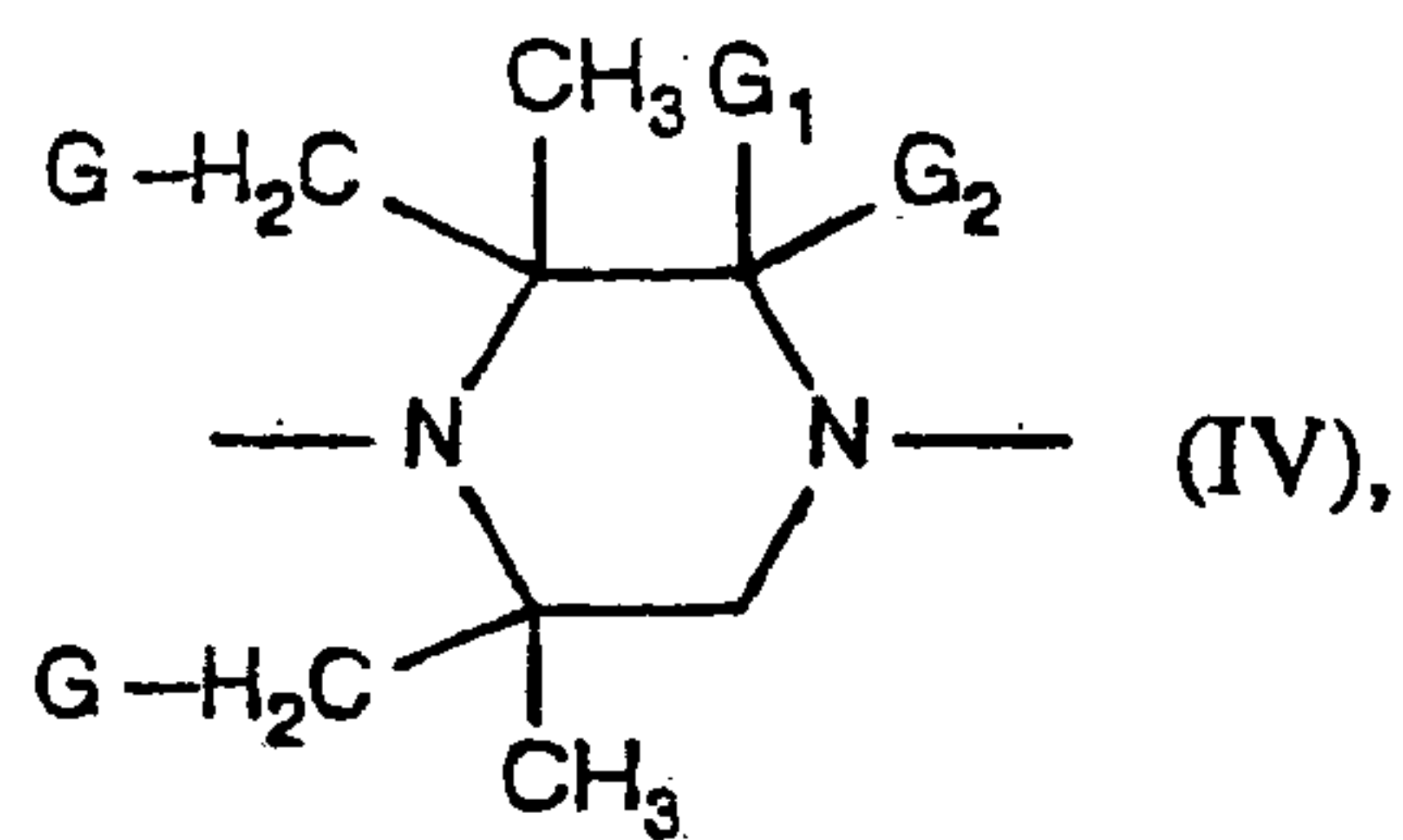
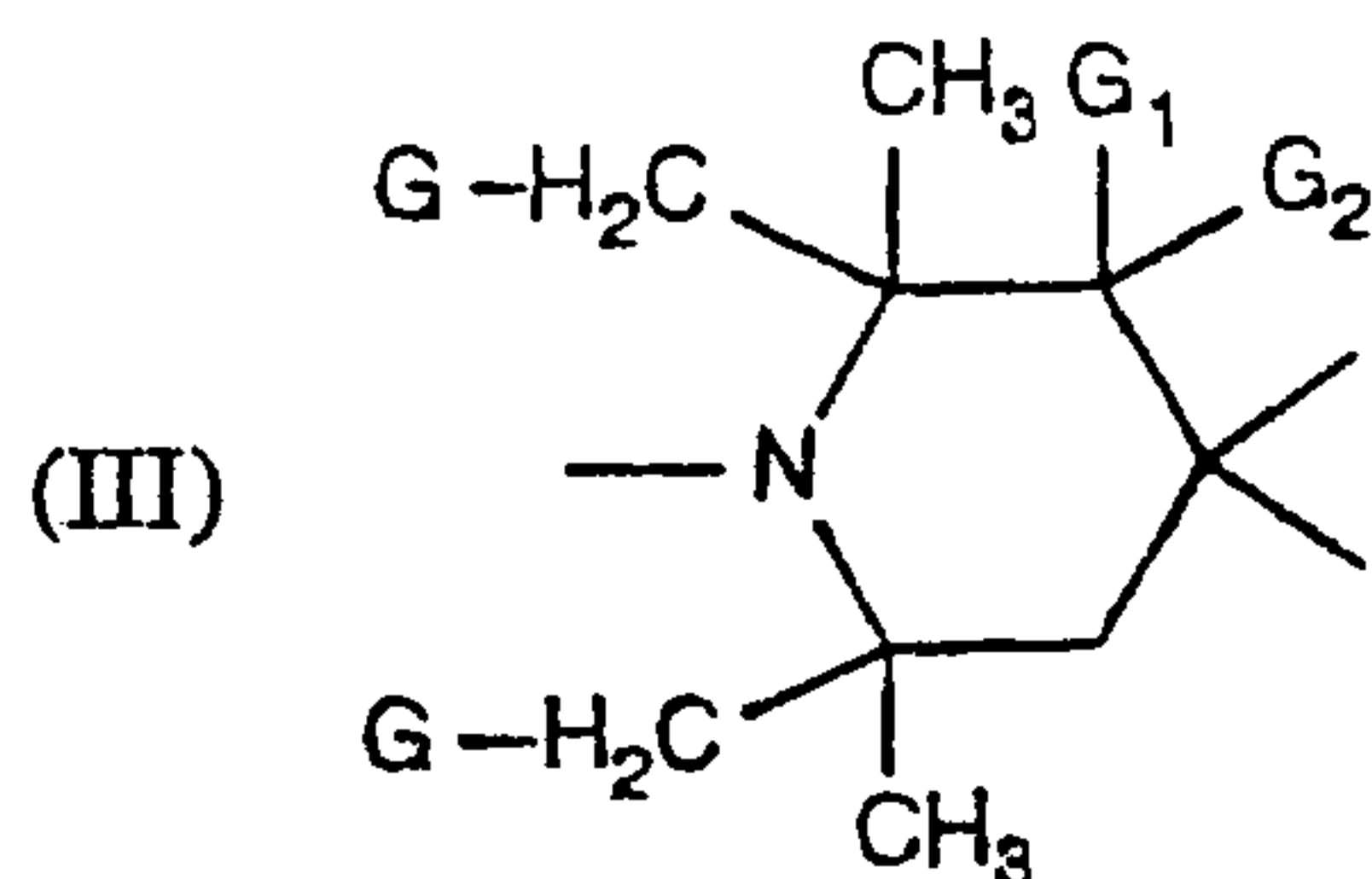
M^{r+} is an r -valent metal cation, and

r is 1, 2 or 3; or

(ii) at least one compound from the group consisting of sterically hindered amines having a molecular weight of greater than 500 and containing at least one radical of the formula III or IV

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- 3 -



in which

G is hydrogen or methyl,

G₁ and G₂ are hydrogen, methyl or together are =O; or

(iii) (x) at least one compound from the group consisting of phenolic antioxidants, and

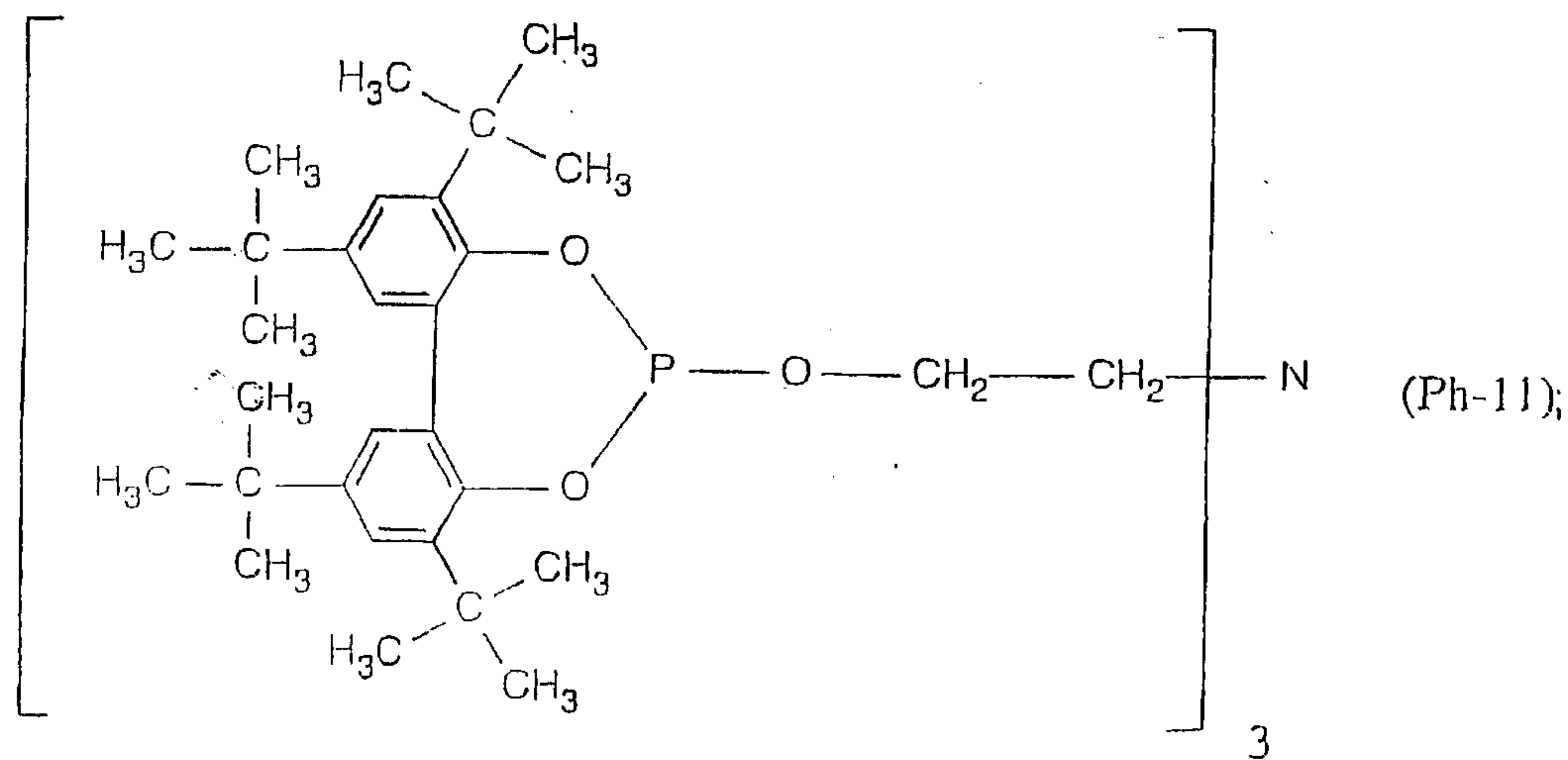
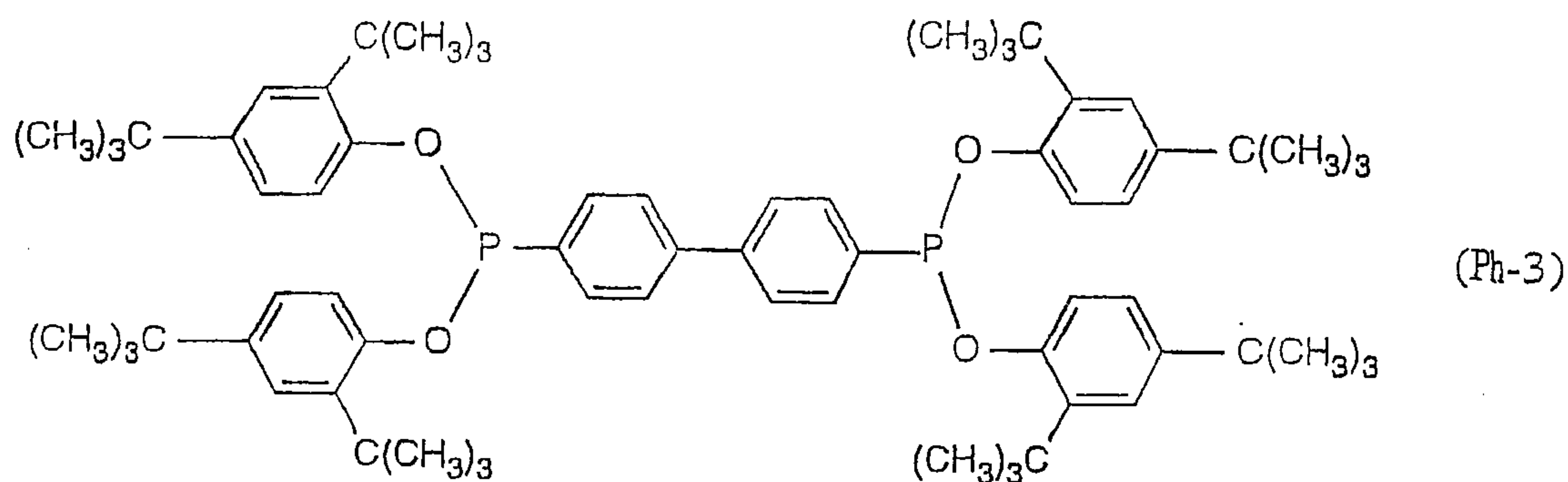
(y) at least one compound from the group consisting of sterically hindered amines having a molecular weight of greater than 500 and containing at least one radical of the formula III or IV.

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-3a-

According to one aspect of the present invention, there is provided a process for stabilizing a thick-walled polyolefin moulding which is in permanent contact with water, which comprises incorporating in or applying to said moulding a mixture of a component (b) in an amount of from 0.02 to 0.6 % based on the weight of the moulding, a component (c) in an amount of from 0.02 to 0.5 % based on the weight of the moulding and a component (d) in an amount of from 0.02 to 1.0 % based on the weight of the moulding, in which

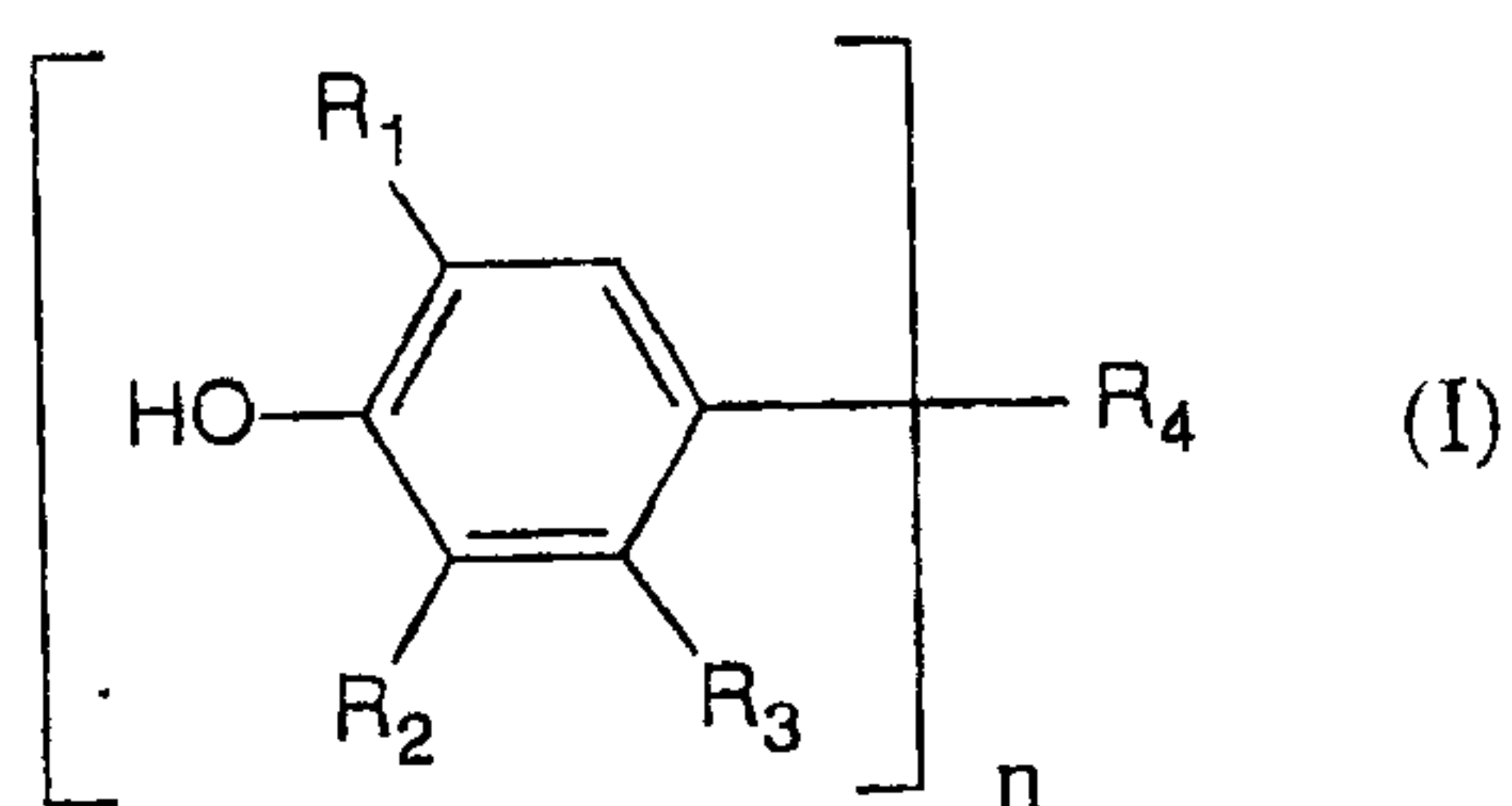
component (b) is tris(2,4-di-tert-butylphenyl) phosphite, bis(2,4-di-tert-butyl-6-methyl) ethyl phosphite or a compound of the formula Ph-3 or Ph-11



component (c) is a compound of the formula I

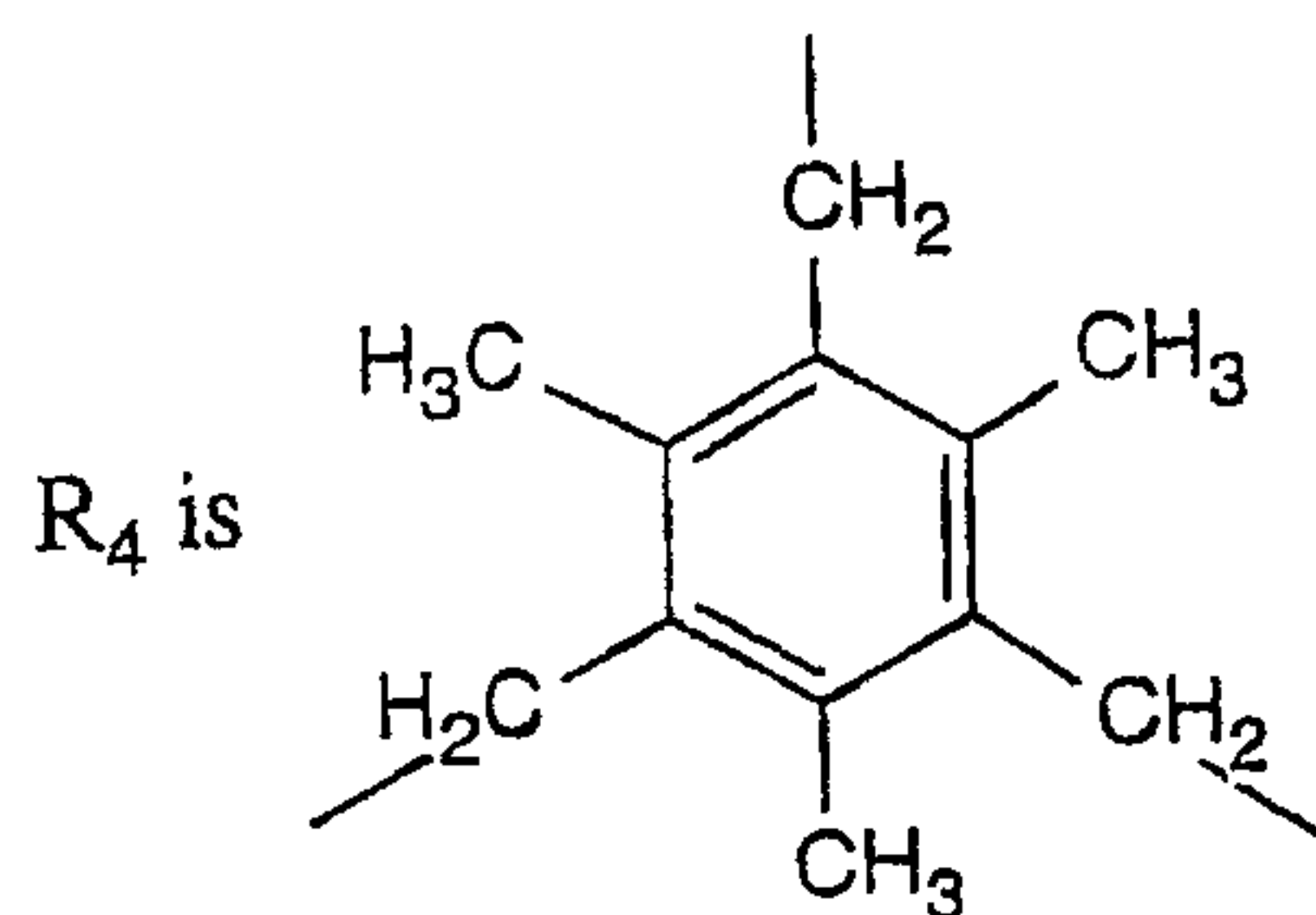
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-3b-

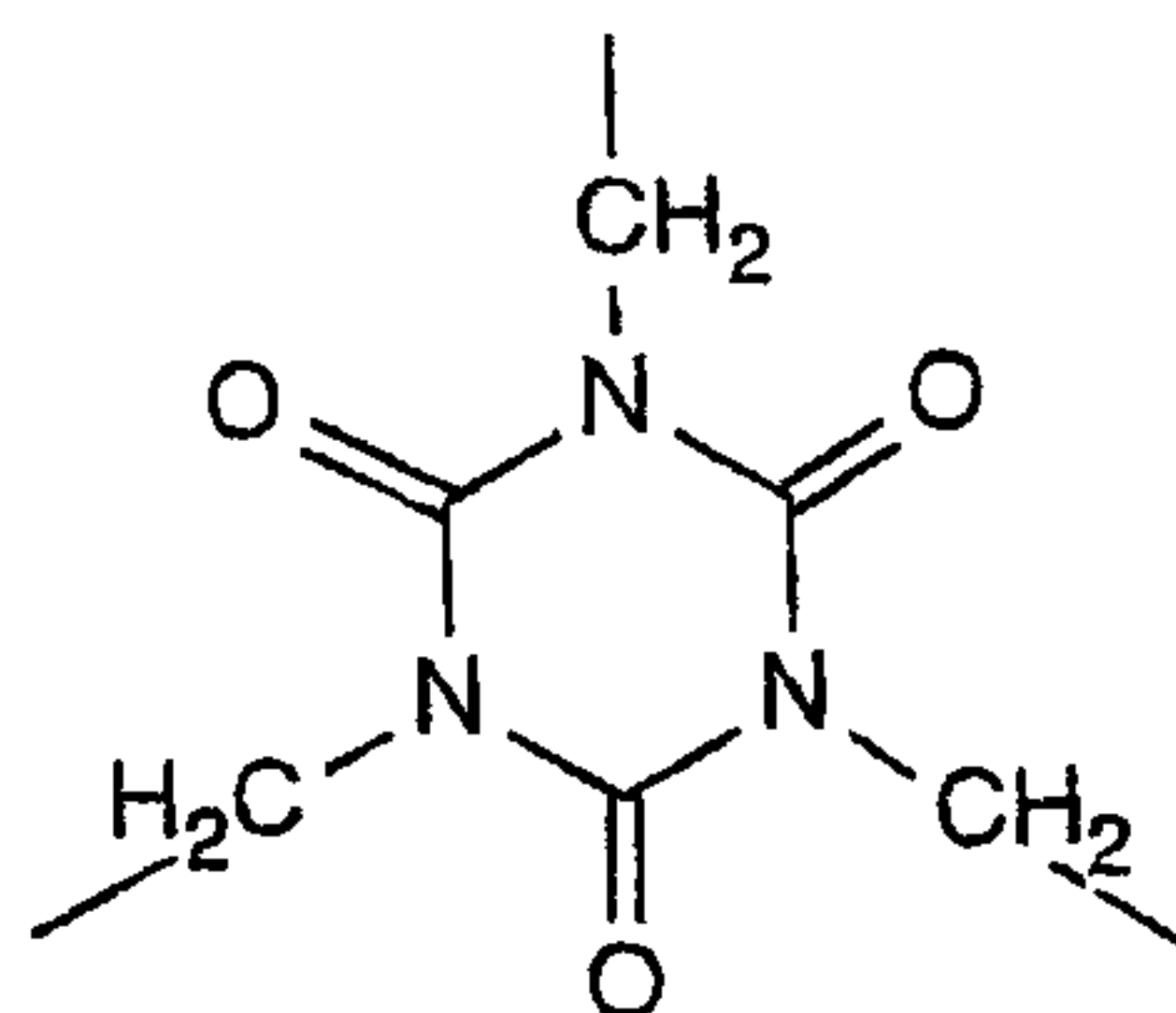


in which

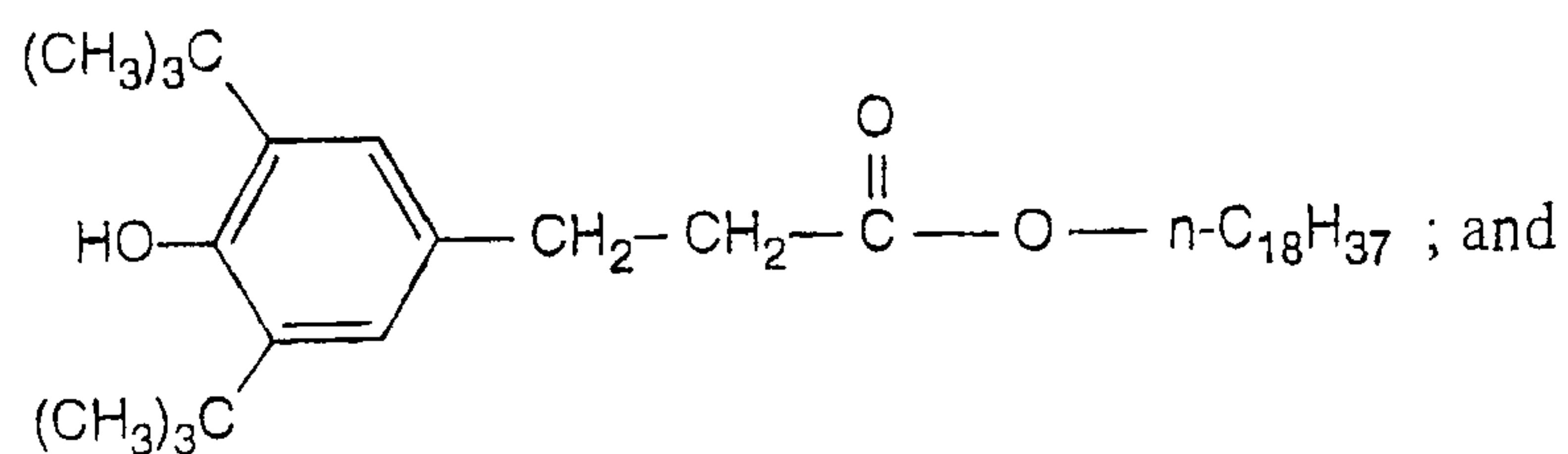
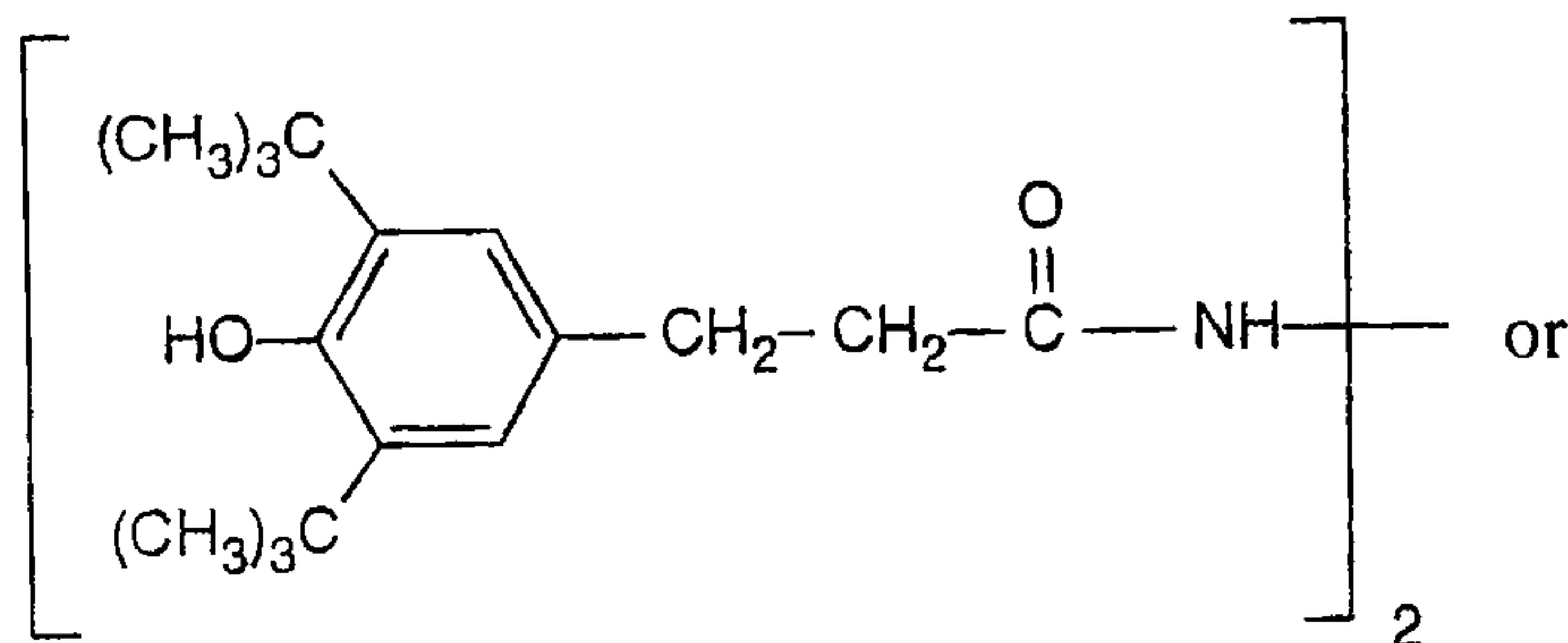
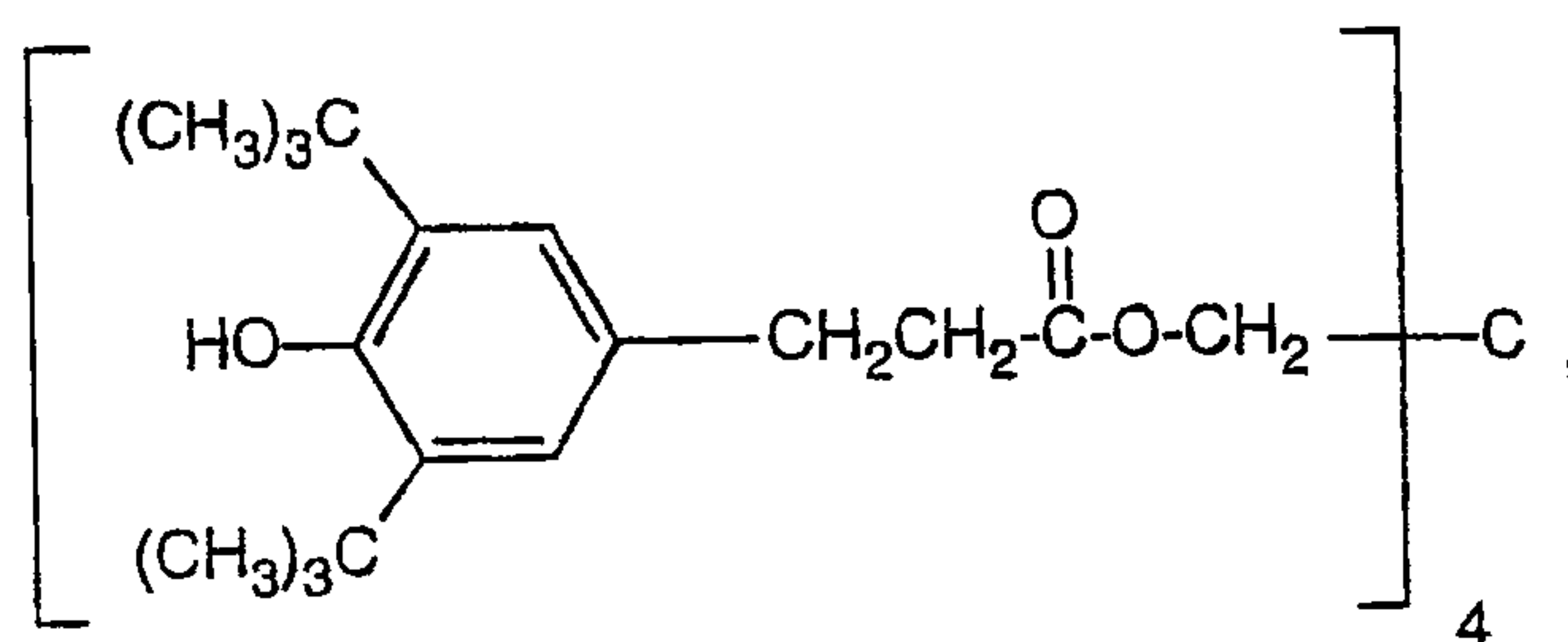
n is 3,

 R_1 and R_2 are tert-butyl, R_3 is hydrogen, and

or



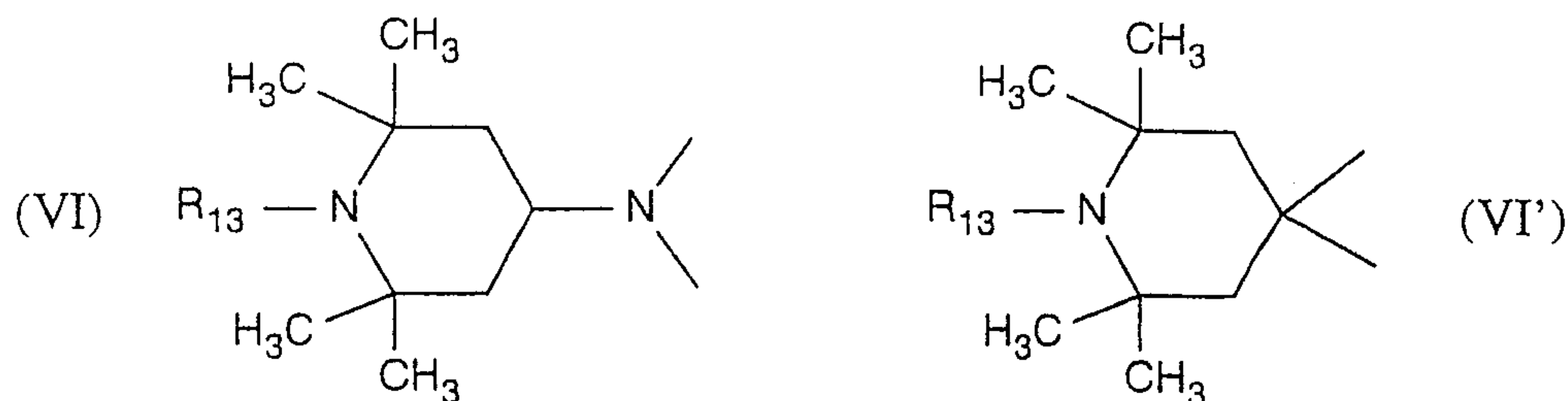
; or in which component (c) is



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-3c-

component (d) is a compound from the group consisting of sterically hindered amines in which the molecular weight is greater than 1000 and the compound contains at least one radical of the formula VI or VI'



in which

R_{13} is hydrogen or methyl.

Alkyl having up to 20 carbon atoms is a branched or unbranched radical, for example methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, eicosyl or docosyl. R_1 and R_2 are preferably C_1 - C_{12} alkyl, in particular C_1 - C_8 alkyl, for example tert-butyl. R_7 is particularly preferably C_1 - C_{12} alkyl, in particular C_1 - C_{10} alkyl, for example C_1 - C_8 alkyl.

Excluded from the compounds that can make up component b) is tris[2-tert-butyl-4-(2-methyl-4-hydroxy-5-tert-butylphenylthio)-5-methyl]-phenyl phosphite.

In the composition of the invention, there is a proviso: if component (a) is poly-1-butene and component (c)(i) is 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, component (b) is not tris(2,4-di-tert-butyl-phenyl)phosphite.

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-3d-

C₅-C₁₂cycloalkyl, in particular C₅-C₈cycloalkyl, is, for example, cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl. Cyclohexyl is preferred.

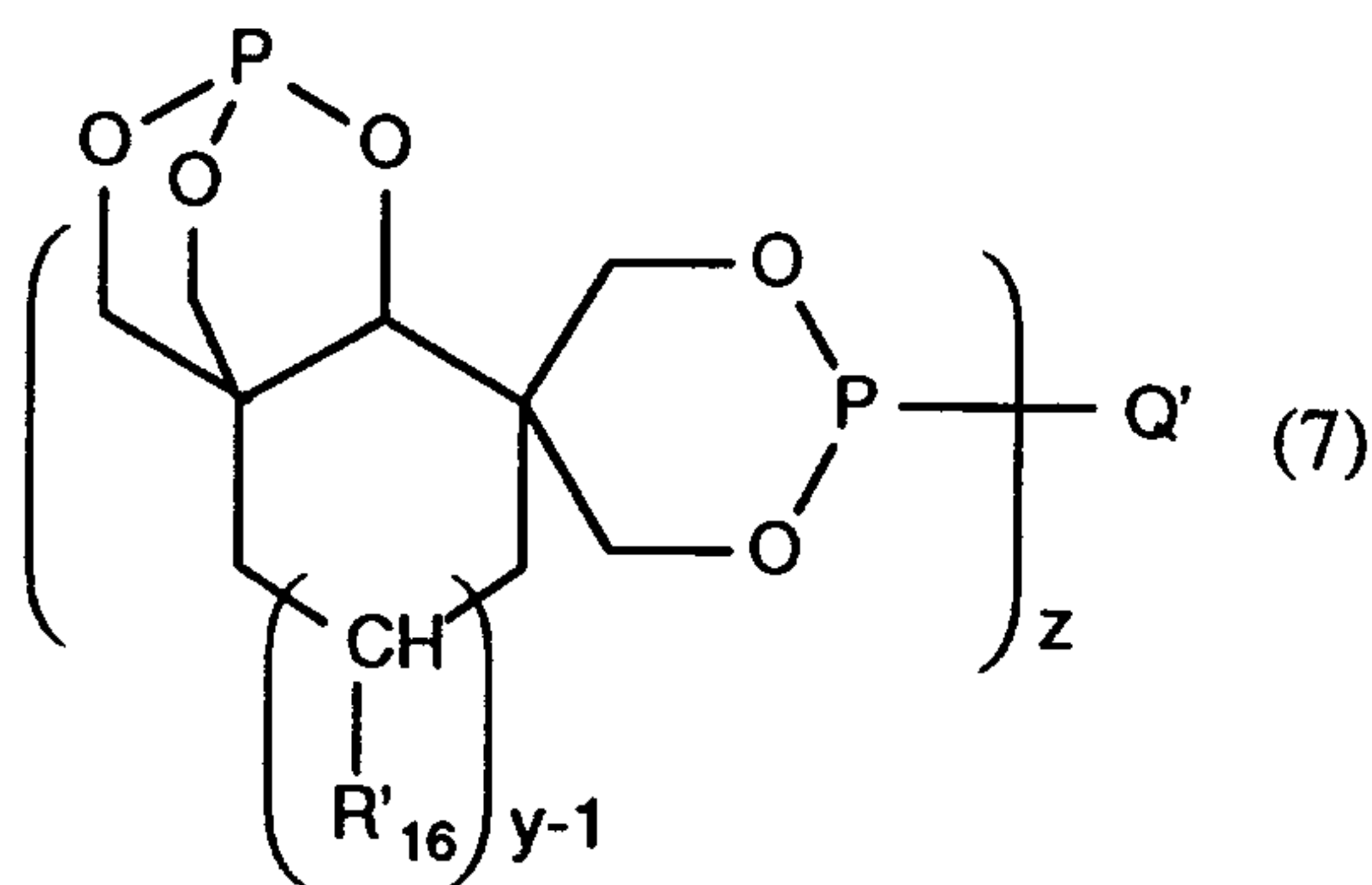
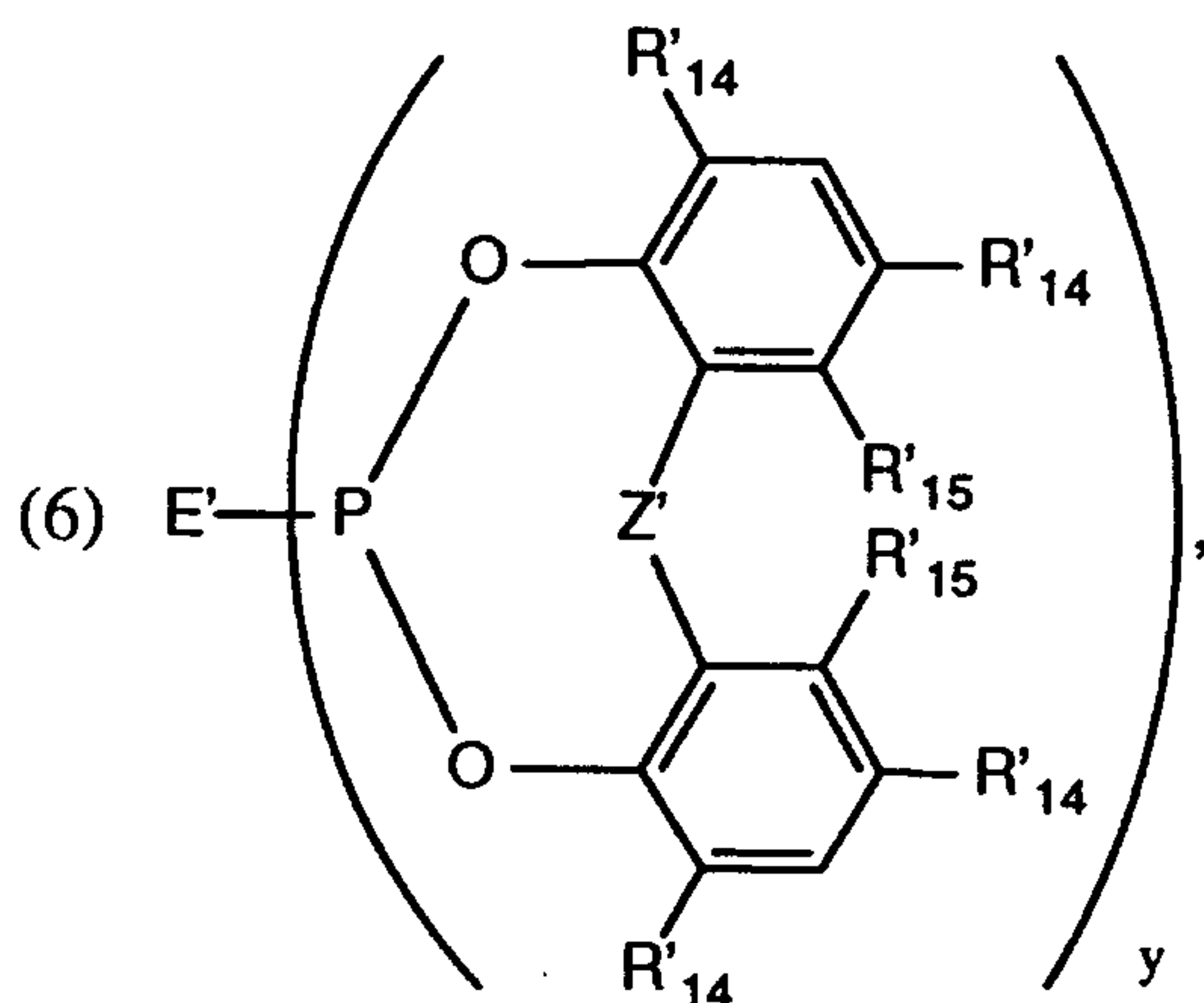
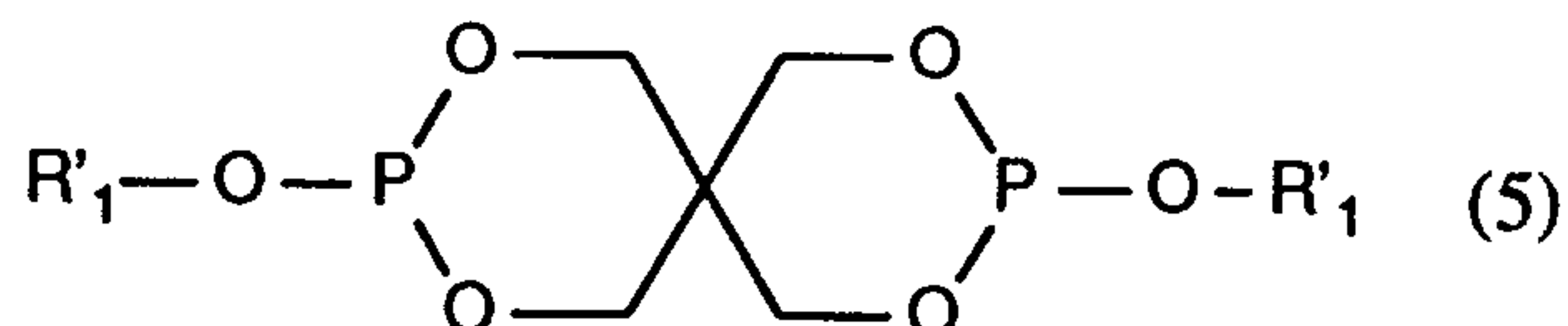
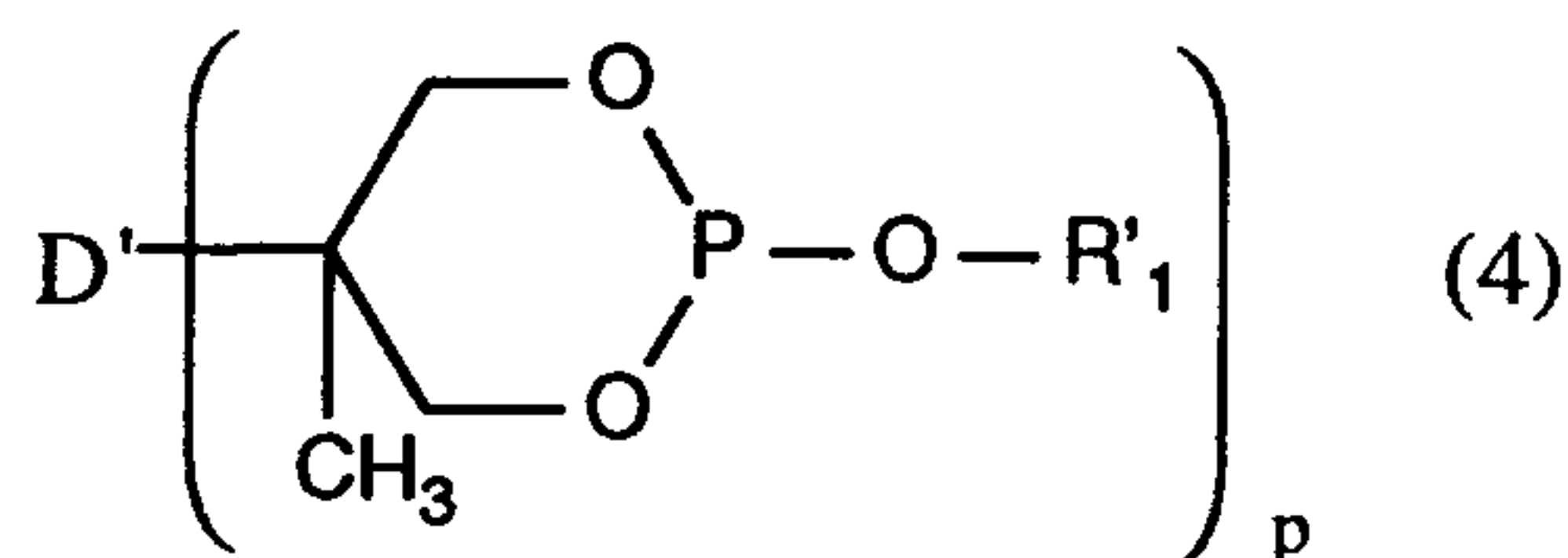
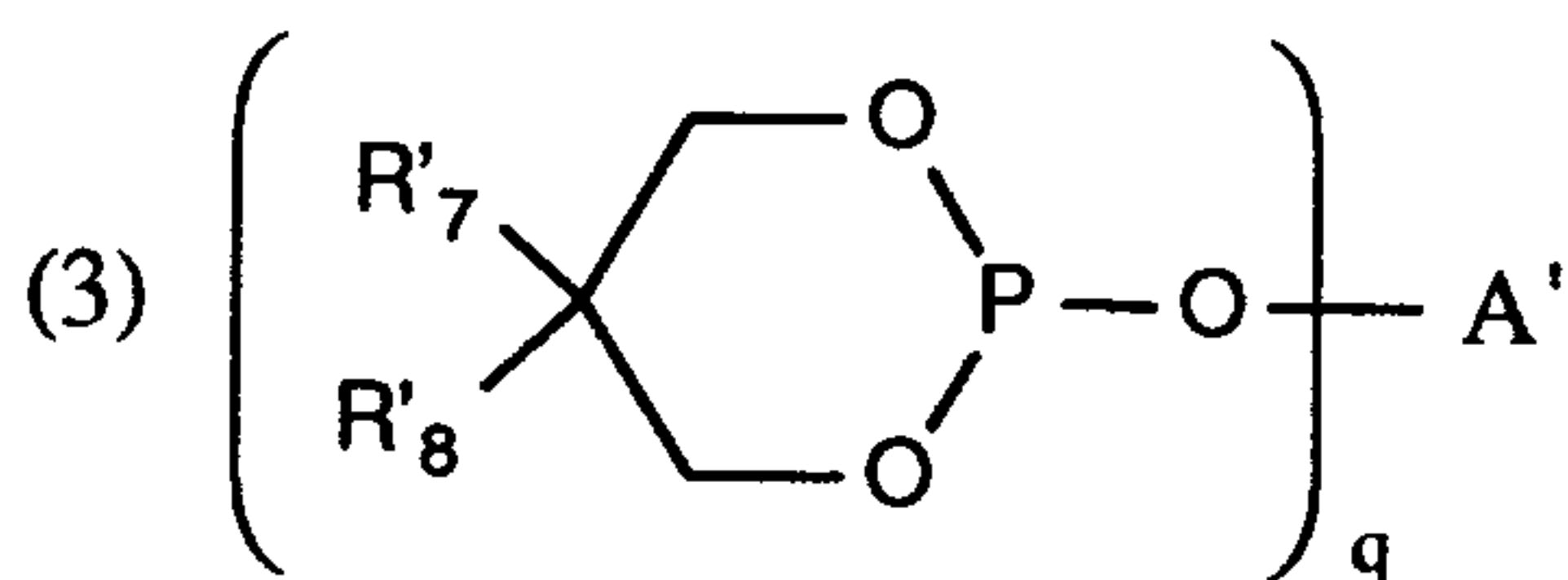
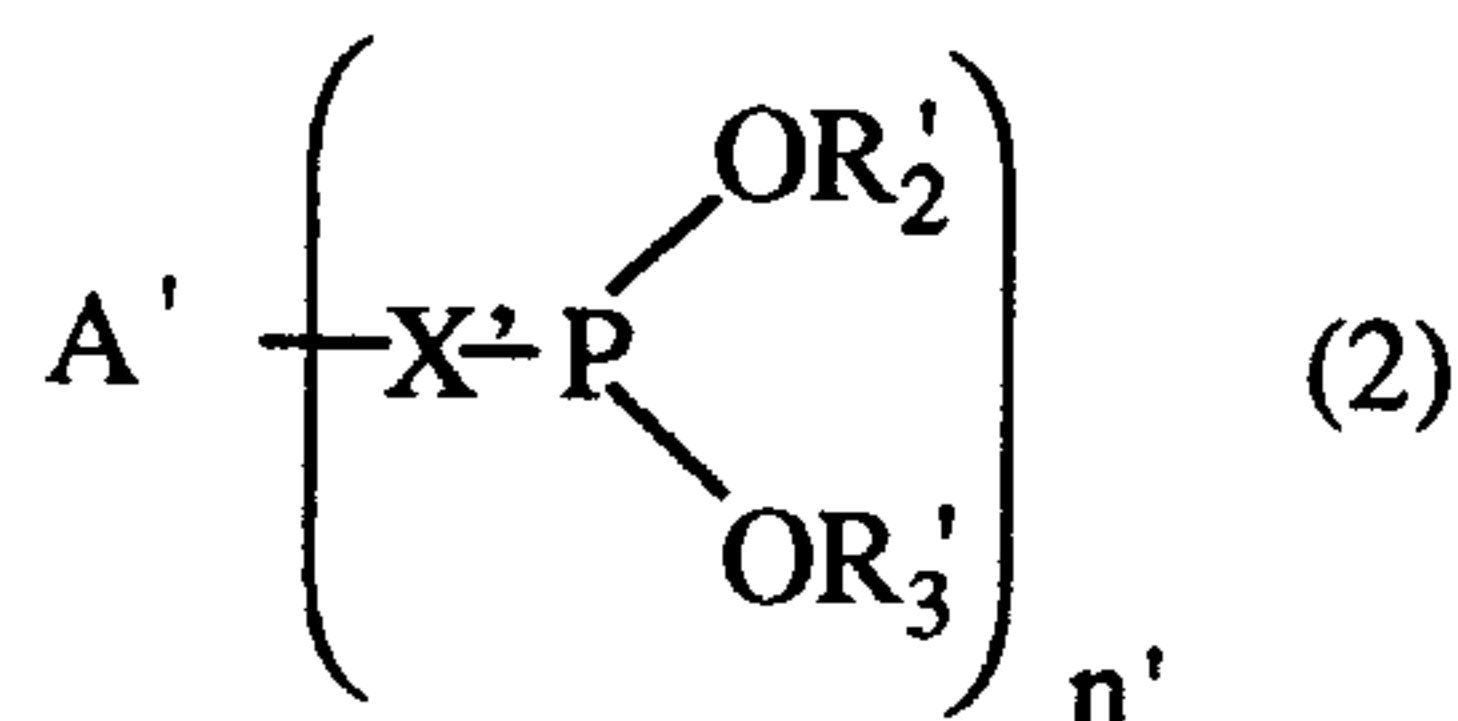
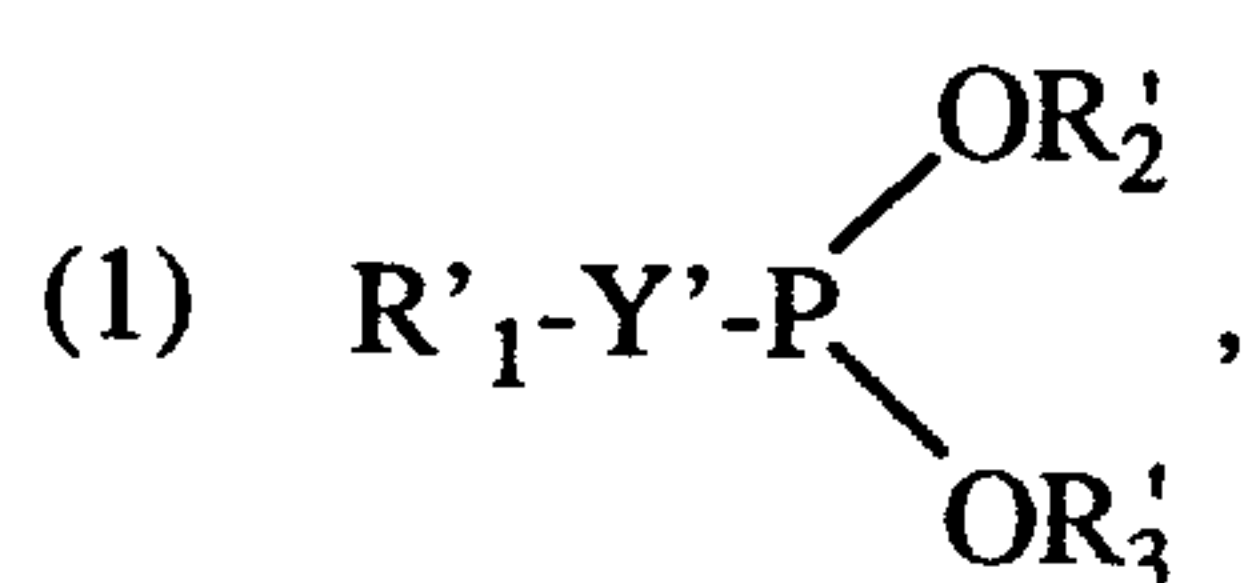
C₇-C₉phenylalkyl is, for example, benzyl, α -methylbenzyl, α,α -dimethylbenzyl or 2-phenylethyl.

C₁-C₄alkyl-substituted phenyl or naphthyl, which preferably contains 1 to 3, in particular 1 or 2, alkyl groups, is, for example, o-, m- or p-methylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, 3,5-dimethylphenyl, 2-methyl-6-ethylphenyl, 4-tert-butylphenyl, 2-ethylphenyl, 2,6-diethylphenyl, 1-methylnaphthyl, 2-methylnaphthyl, 4-methylnaphthyl, 1,6-dimethylnaphthyl or

4-tert-butyl-naphthyl.

A monovalent, divalent or trivalent metal cation is preferably a cation of an alkali metal, alkaline earth metal, heavy metal or aluminium, for example Na^+ , K^+ , Mg^{++} , Ca^{++} , Ba^{++} , Zn^{++} or Al^{+++} . Ca^{++} is particularly preferred.

Of interest are compositions in which component (b) is an organic phosphite or phosphonite of the formula (1) to (7)

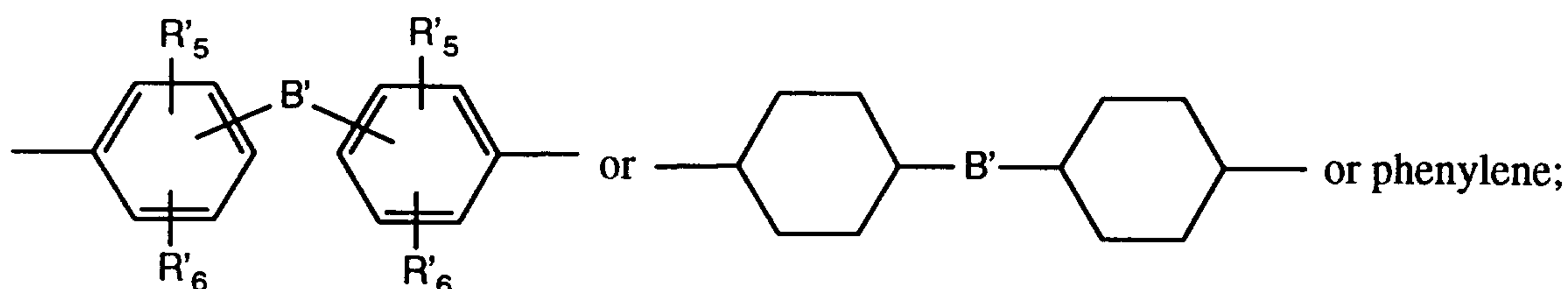


in which the indices are integers and

n' is 2, 3 or 4; p is 1 or 2; q is 2 or 3; r is 4 to 12; y is 1, 2 or 3; and z is 1 to 6;

A' , if n' is 2, is alkylene having 2 to 18 carbon atoms; alkylene having 2 to 12 carbon

atoms which is interrupted by -S-, -O- or -NR'₄-; a radical of the formula



A', if n' is 3, is a radical of the formula -C_rH_{2r-1}-;

A', if n' is 4, is the radical of the formula C(CH₂)₄-;

A'' is as defined for A' if n' is 2;

B' is a radical of the formula -CH₂-; -CHR'₄-; -CR'₁R'₄-; -S- or a direct bond; or C₅-C₇cycloalkylidene; or cyclohexylidene which is substituted by 1 to 4 C₁-C₄alkyl radicals in position 3, 4 and/or 5;

D', if p is 1, is methyl and, if p is 2, is -CH₂OCH₂-;

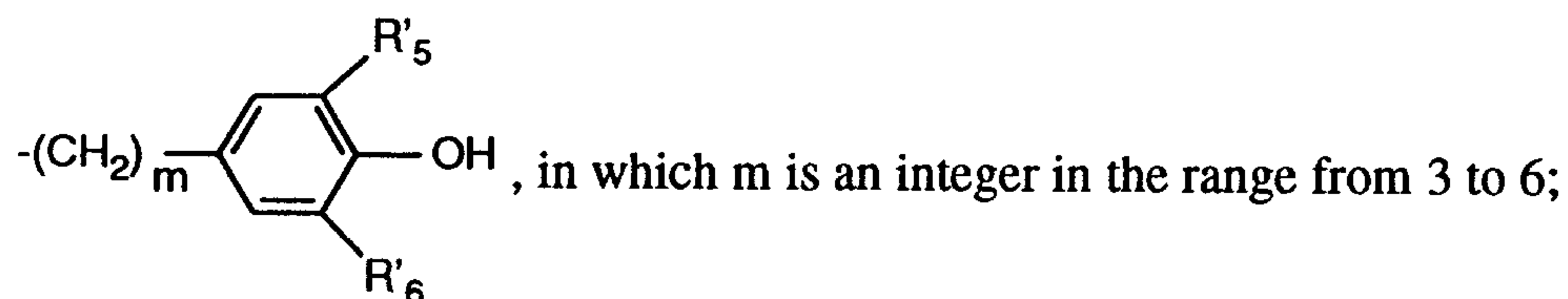
E', if y is 1, is alkyl having 1 to 18 carbon atoms, a radical of the formula -OR'₁ or halogen;

E', if y is 2, is a radical of the formula -O-A''-O-;

E', if y is 3, is a radical of the formula R'₄C(CH₂O)₃-;

Q' is the radical of an at least z-valent alcohol or phenol, this radical being bonded to the P atom(s) via the alcoholic or phenolic O atom(s);

R'₁, R'₂ and R'₃, independently of one another, are alkyl having 1 to 30 carbon atoms; alkyl having 1 to 18 carbon atoms which is substituted by halogen, -COOR'₄, -CN or -CONR'₄R'₄; alkyl having 2 to 18 carbon atoms which is interrupted by -S-, -O- or -NR'₄-; phenyl-C₁-C₄-alkyl; cycloalkyl having 5 to 12 carbon atoms; phenyl or naphthyl; phenyl or naphthyl which is substituted by halogen, 1 to 3 alkyl radicals or alkoxy radicals having a total of 1 to 18 carbon atoms or phenyl-C₁-C₄alkyl; or a radical of the formula



each R'₄, independently of the others, is hydrogen; alkyl having 1 to 18 carbon atoms, cycloalkyl having 5 to 12 carbon atoms; or phenylalkyl having 1 to 4 carbon atoms in the alkyl moiety;

R'₅ and R'₆, independently of one another, are hydrogen; alkyl having 1 to 8 carbon atoms or cycloalkyl having 5 or 6 carbon atoms;

R'₇ and R'₈, in the case where q = 2, are, independently of one another, C₁-C₄alkyl or

together are a 2,3-dehydropentamethylene radical; and
 R'_7 and R'_8 , in the case where $q = 3$, are methyl;
the substituents R'_{14} , independently of one another, are hydrogen; alkyl having 1 to 9 carbon atoms or cyclohexyl;
the substituents R'_{15} , independently of one another, are hydrogen or methyl; and
 R'_{16} is hydrogen or C_1 - C_4 alkyl, and in the case where a plurality of radicals R'_{16} are present, the radicals R'_{16} are identical or different;
 X' and Y' are each a direct bond or $-O-$; and
 Z' is a direct bond; $-CH_2-$; $-C(R'_{16})_2-$ or $-S-$.

Of particular interest are compositions comprising as component (b) a phosphite or phosphonite of the formula (1), (2), (5) or (6) in which
 n' is the number 2 and y is the number 1 or 2;
 A' is alkylene having 2 to 18 carbon atoms; p-phenylene or p-biphenylene;
 E' , in the case where $y = 1$, is C_1 - C_{18} alkyl, $-OR_1$ or fluorine; and in the case where $y = 2$, is p-biphenylene;
 R'_1 , R'_2 and R'_3 , independently of one another, are alkyl having 1 to 18 carbon atoms; phenyl- C_1 - C_4 alkyl; cyclohexyl; phenyl; or phenyl which is substituted by 1 to 3 alkyl radicals having a total of 1 to 18 carbon atoms;
the substituents R'_{14} independently of one another, are hydrogen or alkyl having 1 to 9 carbon atoms;
 R'_{15} is hydrogen or methyl;
 X' is a direct bond;
 Y' is $-O-$; and
 Z' is a direct bond or $-CH(R'_{16})-$.

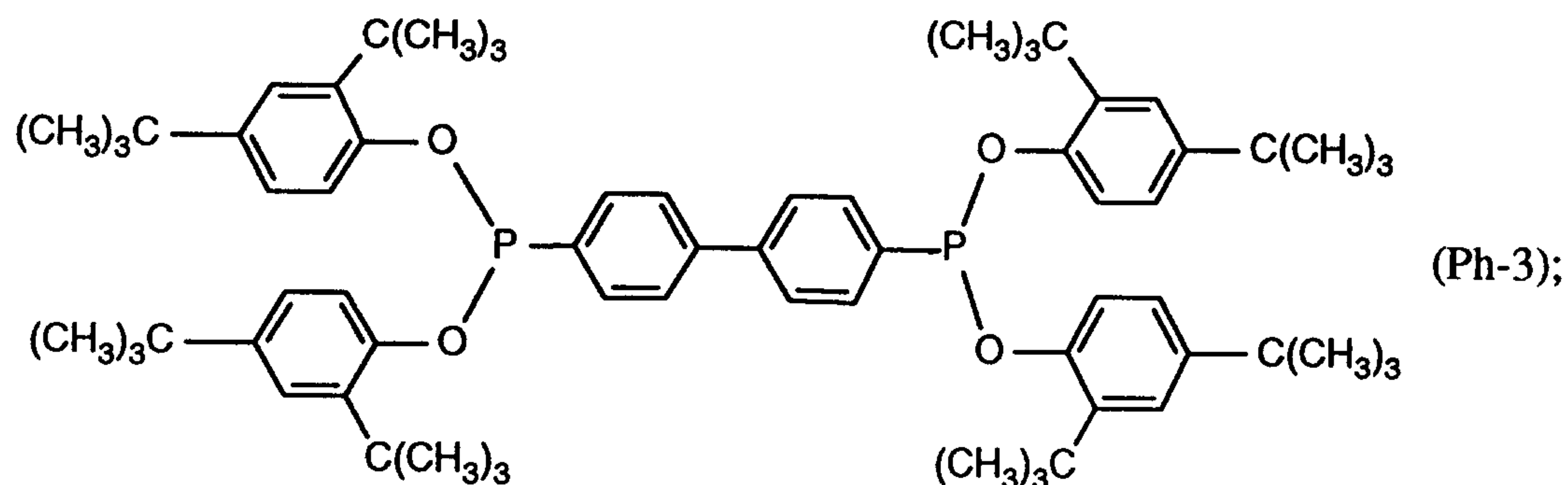
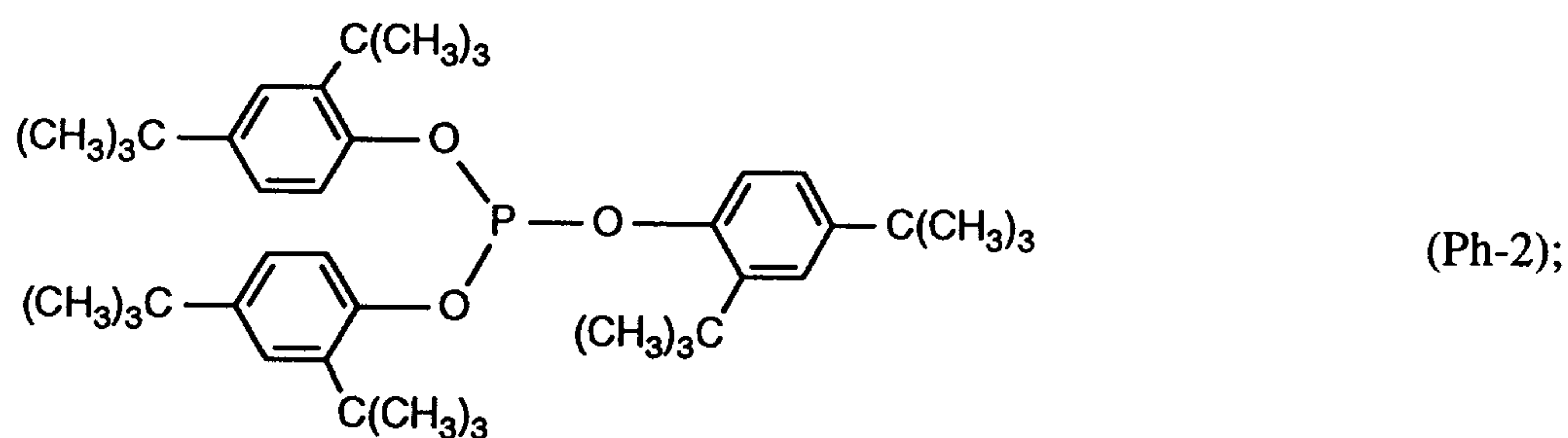
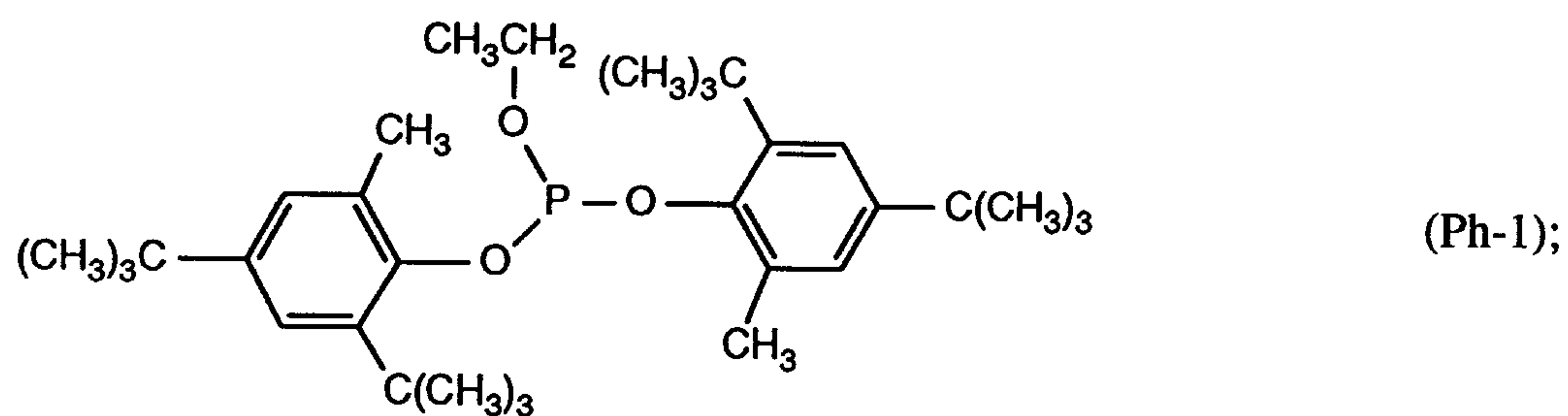
Also of interest are compositions comprising as component (b) a phosphite or phosphonite of the formula (1), (2), (5) or (6) in which
 n' is the number 2 and y is the number 1;
 A' is p-biphenylene;
 E' is C_1 - C_{18} alkoxy or fluorine;
 R'_1 , R'_2 and R'_3 , independently of one another, are alkyl having 1 to 18 carbon atoms; or phenyl which is substituted by 2 or 3 alkyl radicals having a total of 2 to 12 carbon atoms;
the substituents R'_{14} , independently of one another, are methyl or tert-butyl;
 R'_{15} is hydrogen;
 X' is a direct bond;

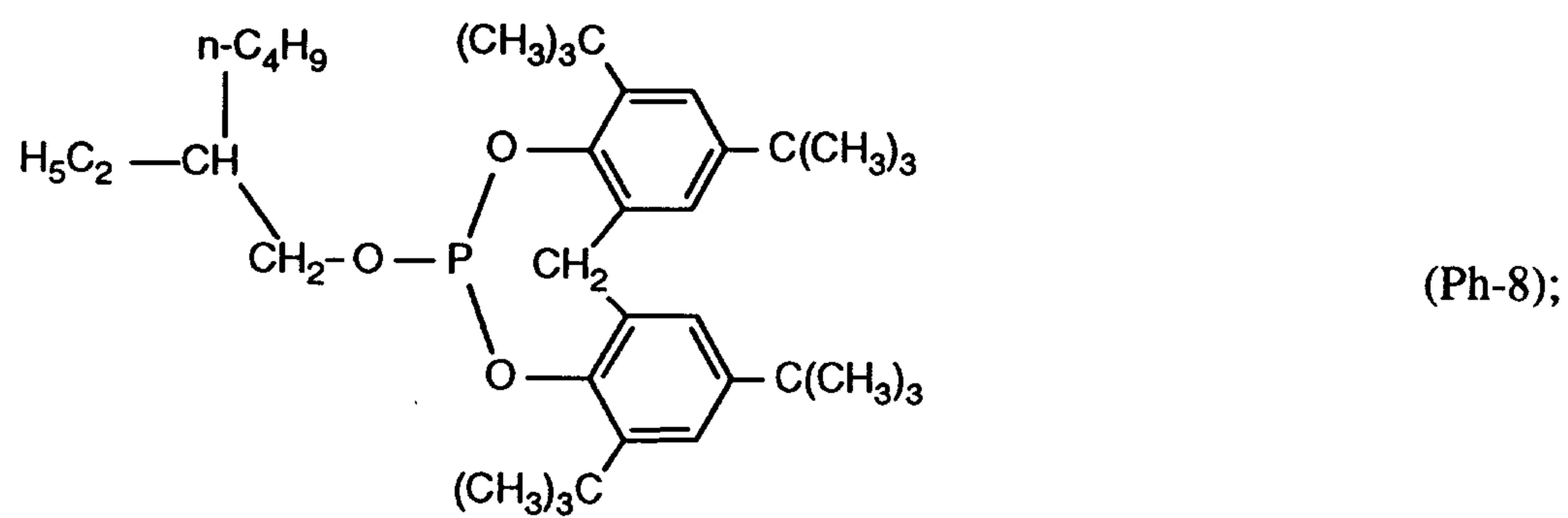
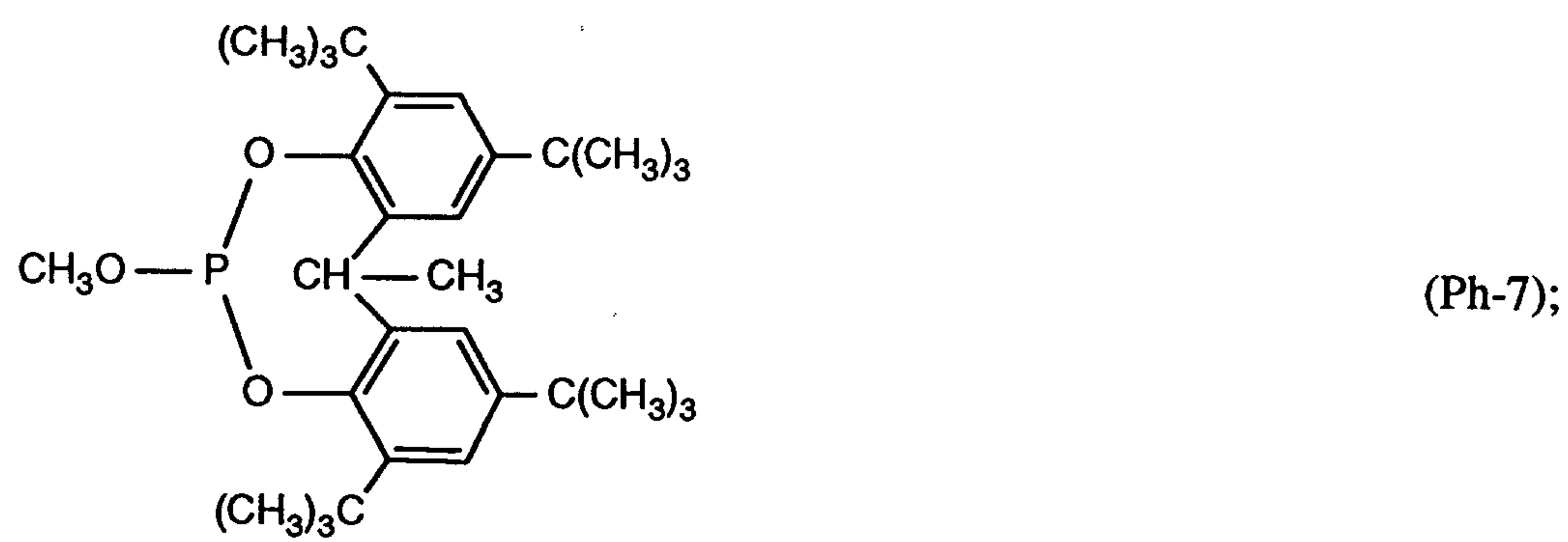
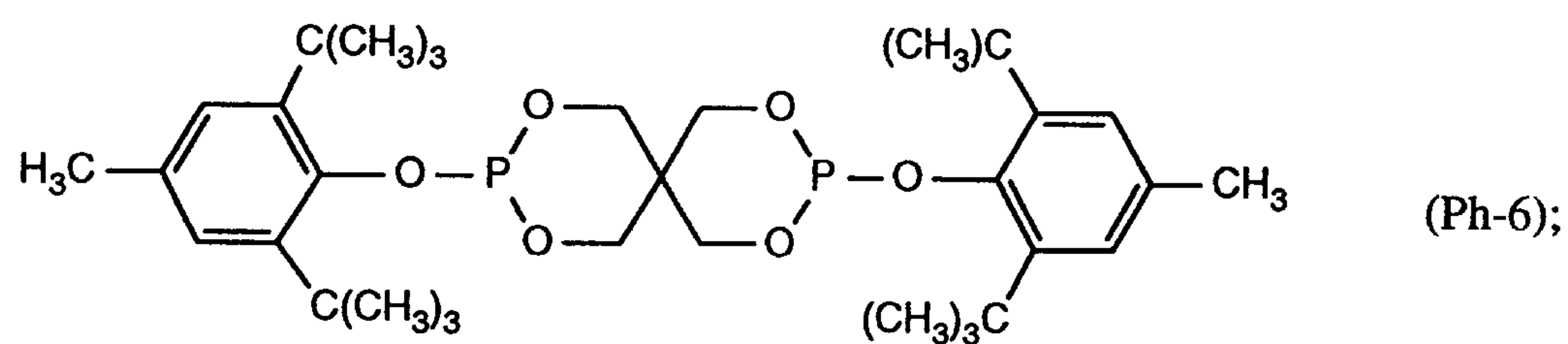
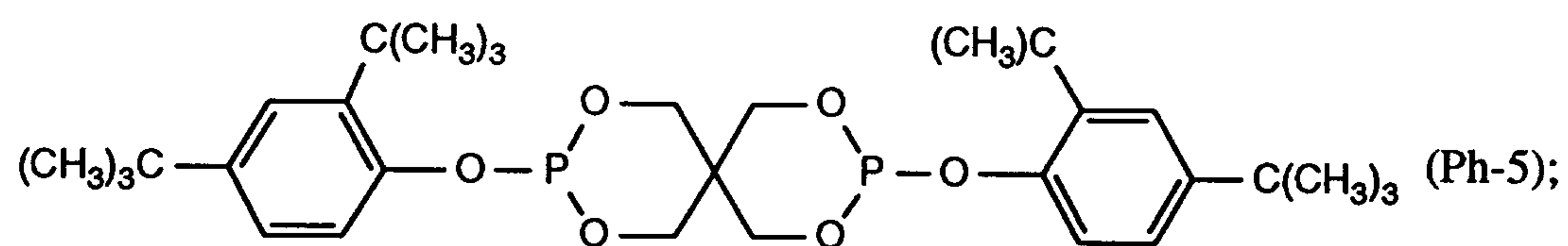
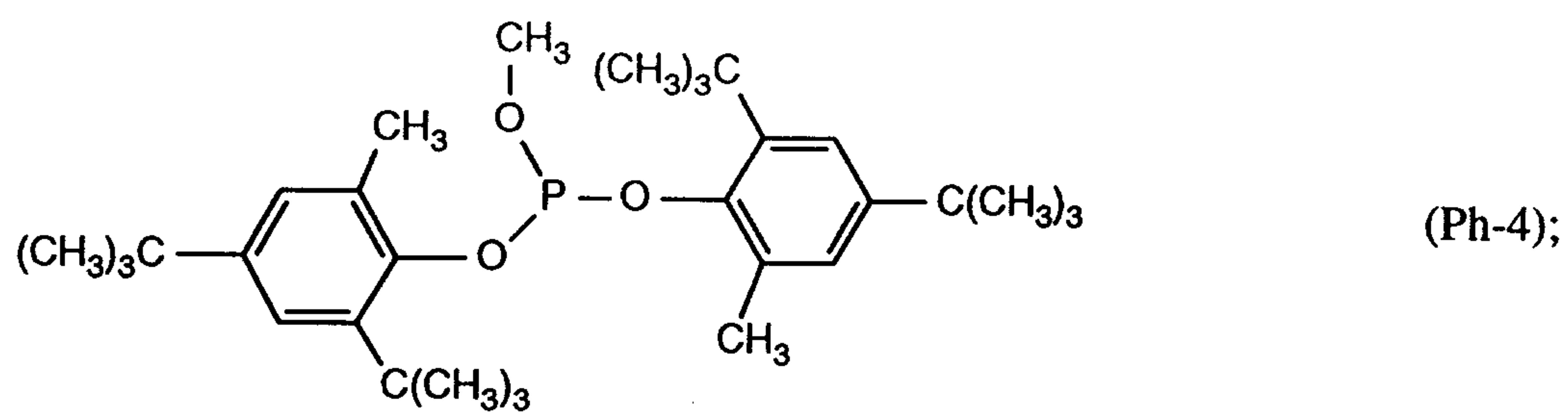
Y' is -O-; and

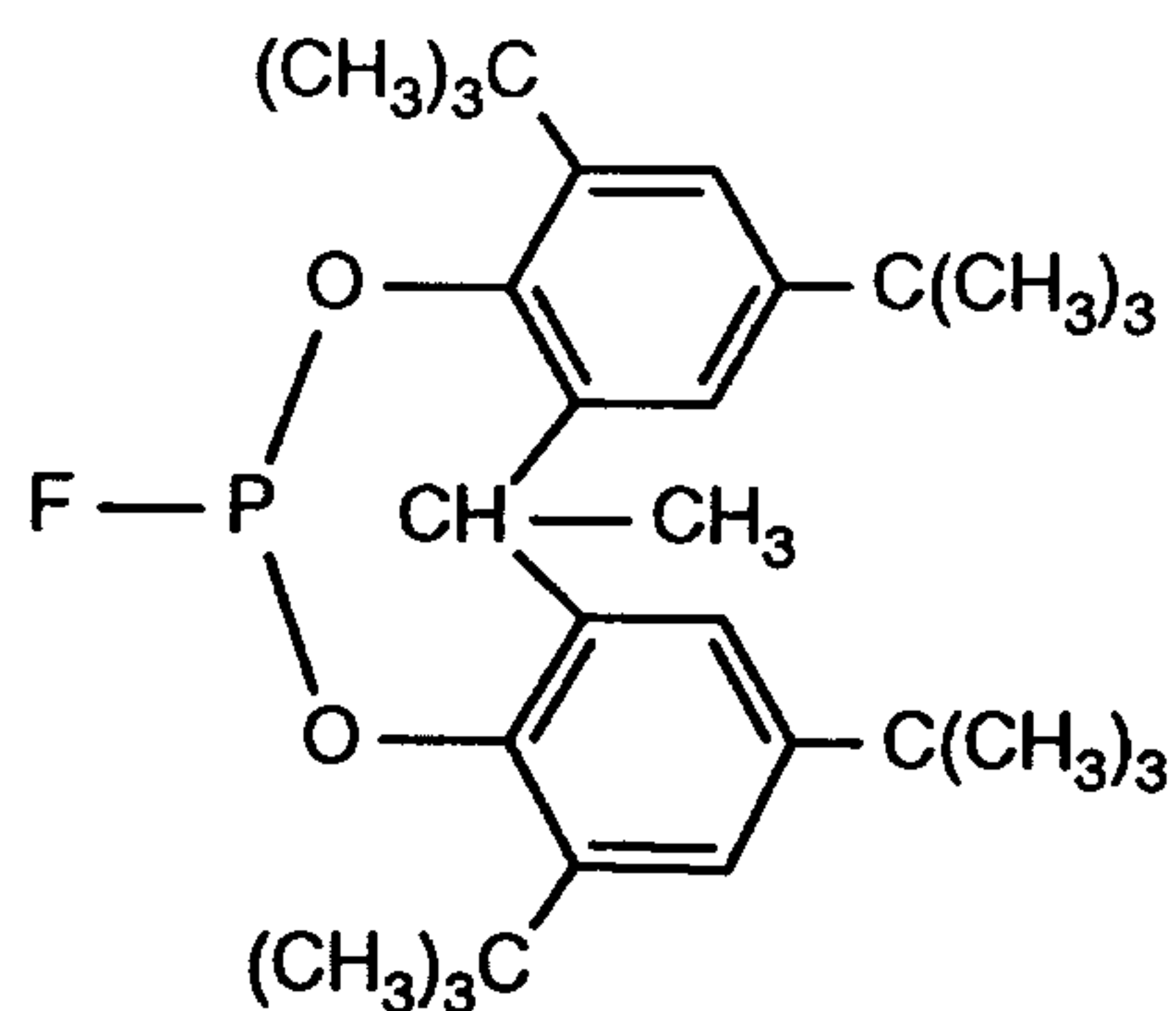
Z' is a direct bond, -CH₂- or -CH(CH₃)-.

Particular preference is given to compositions comprising as component (b) a phosphite, in particular of the formula (1) or (5).

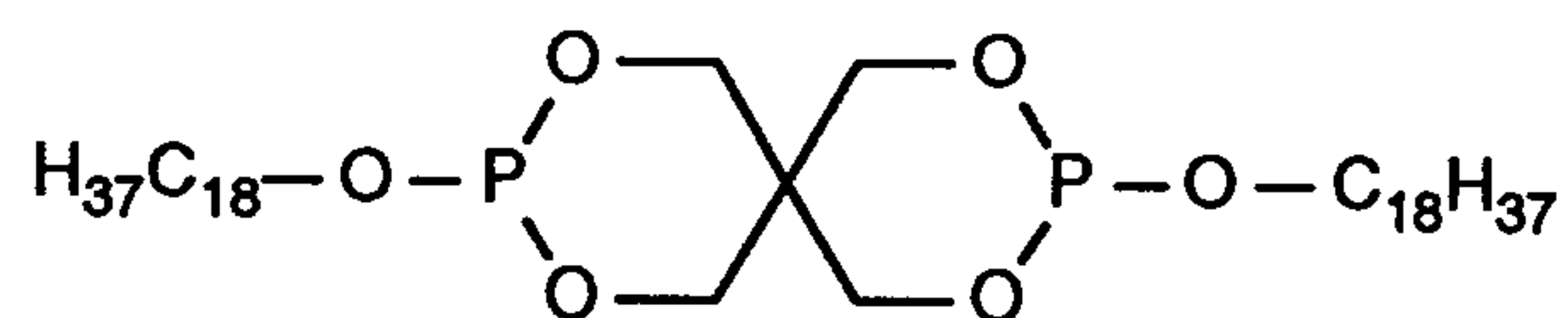
The following compounds are examples of phosphites or phosphonites which are particularly suitable as component (b) in the novel composition:



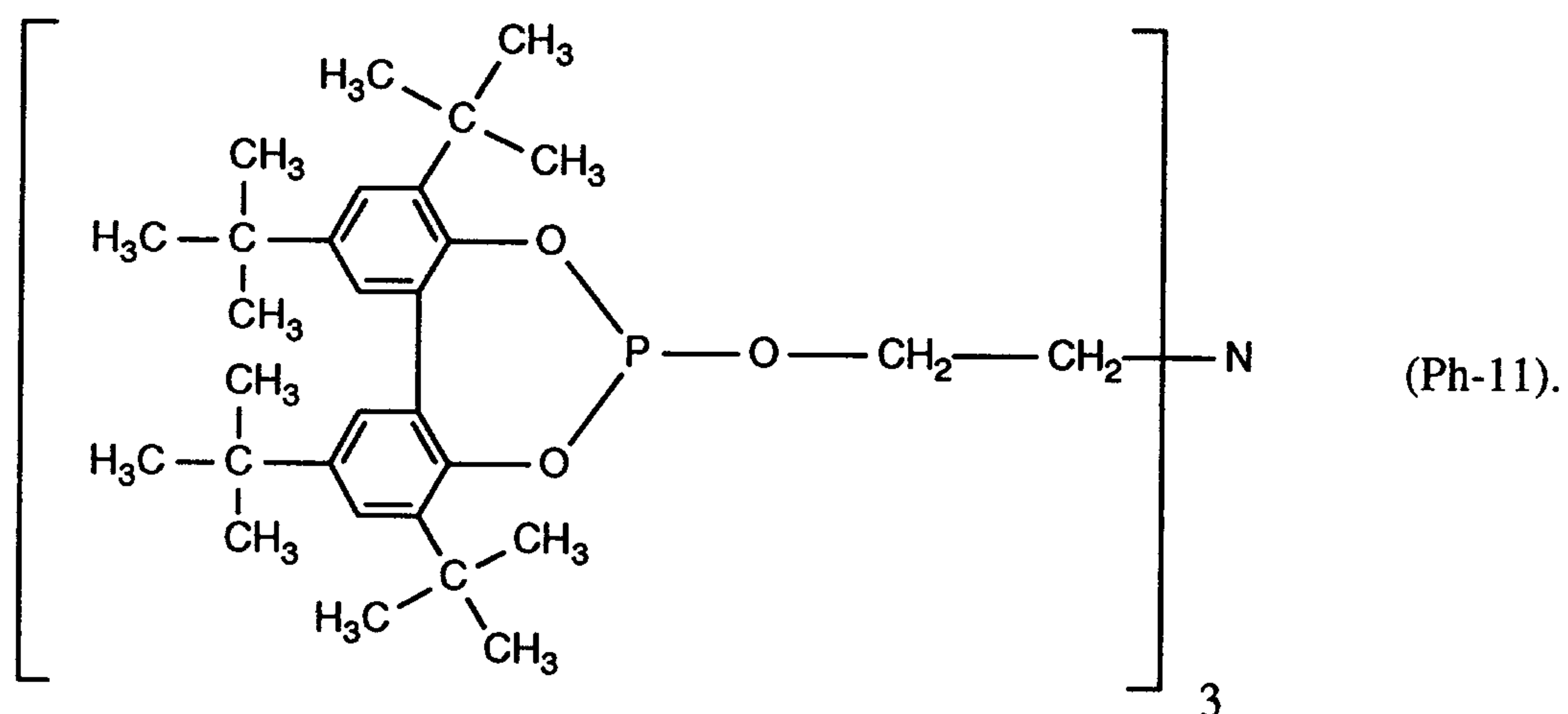




(Ph-9);



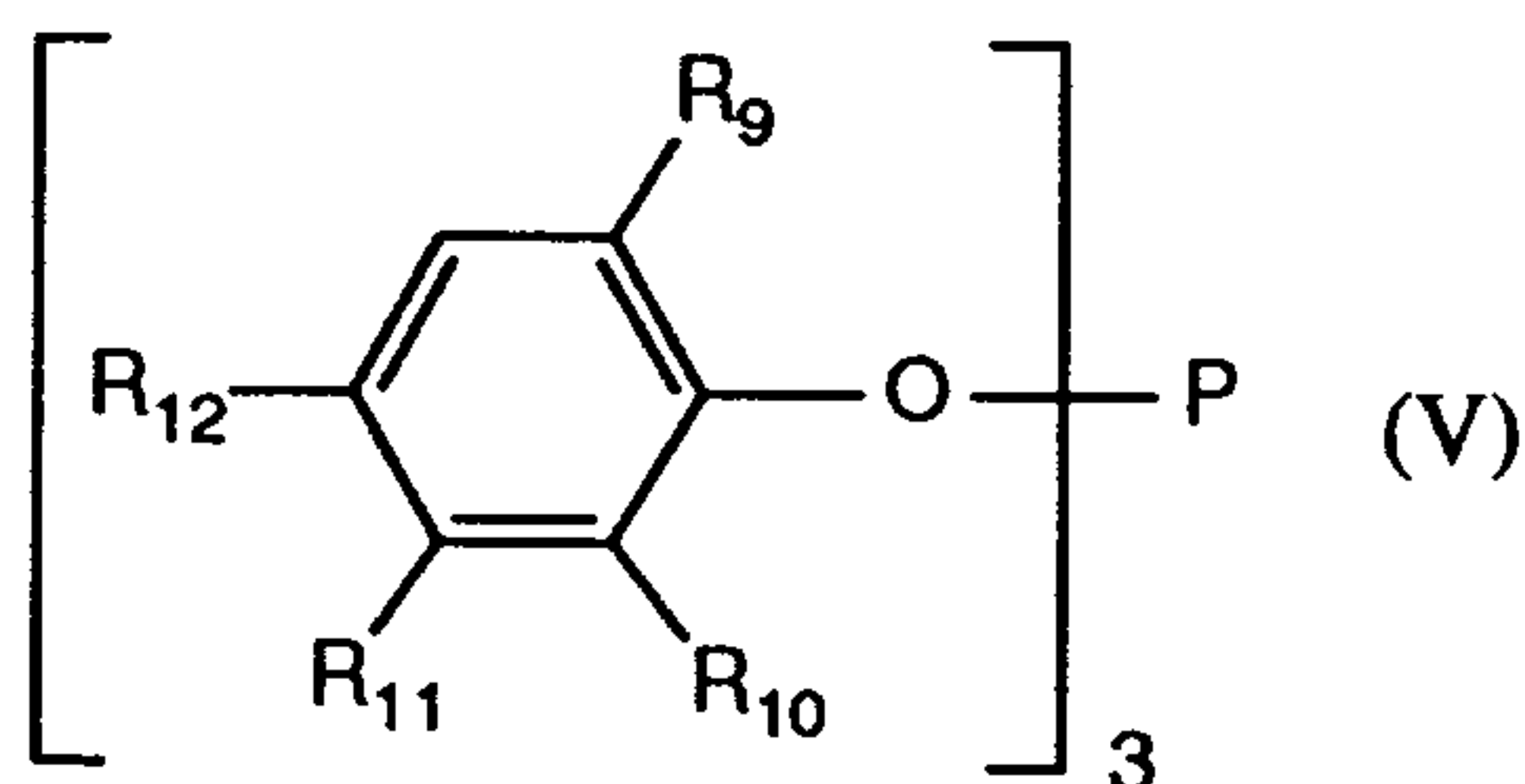
(Ph-10);

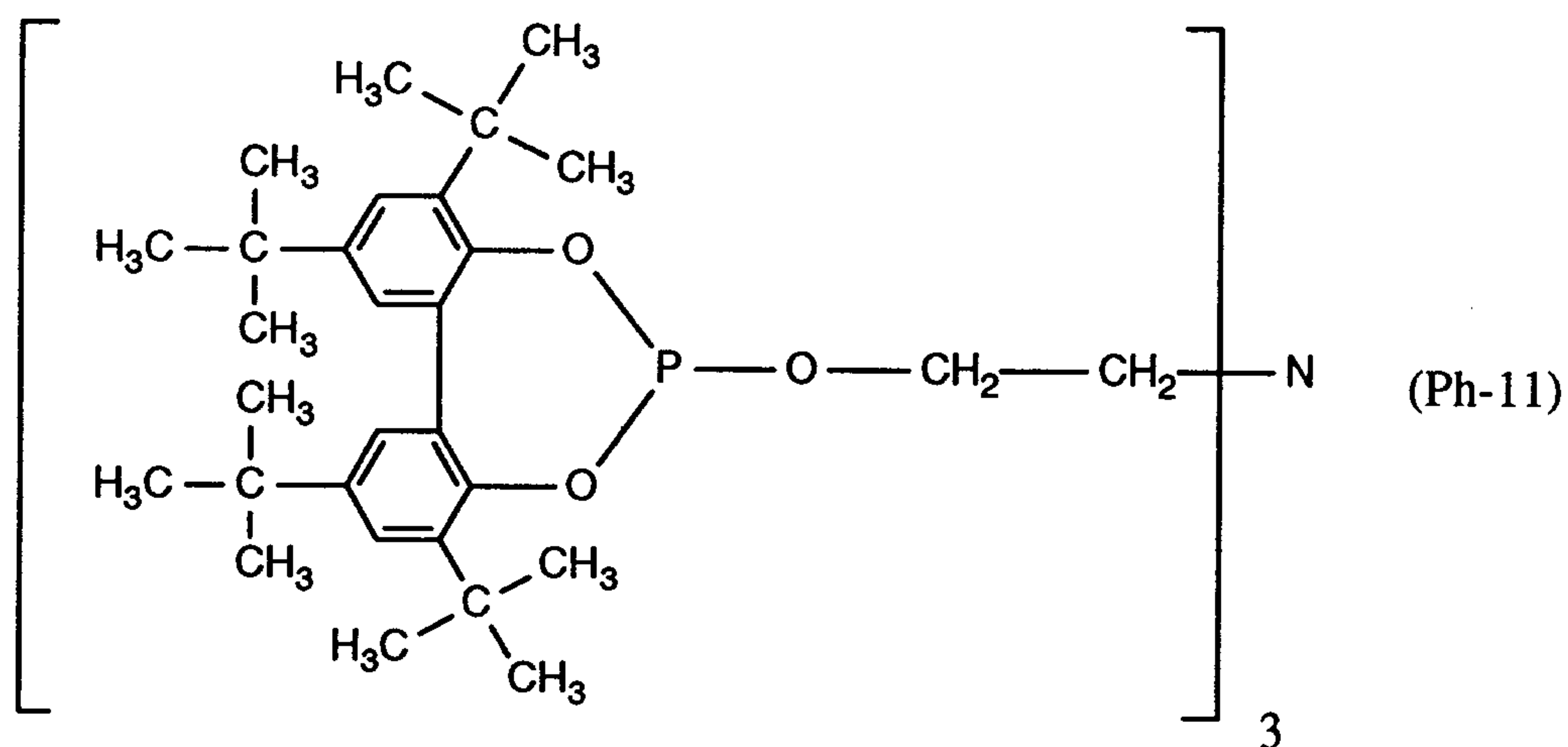
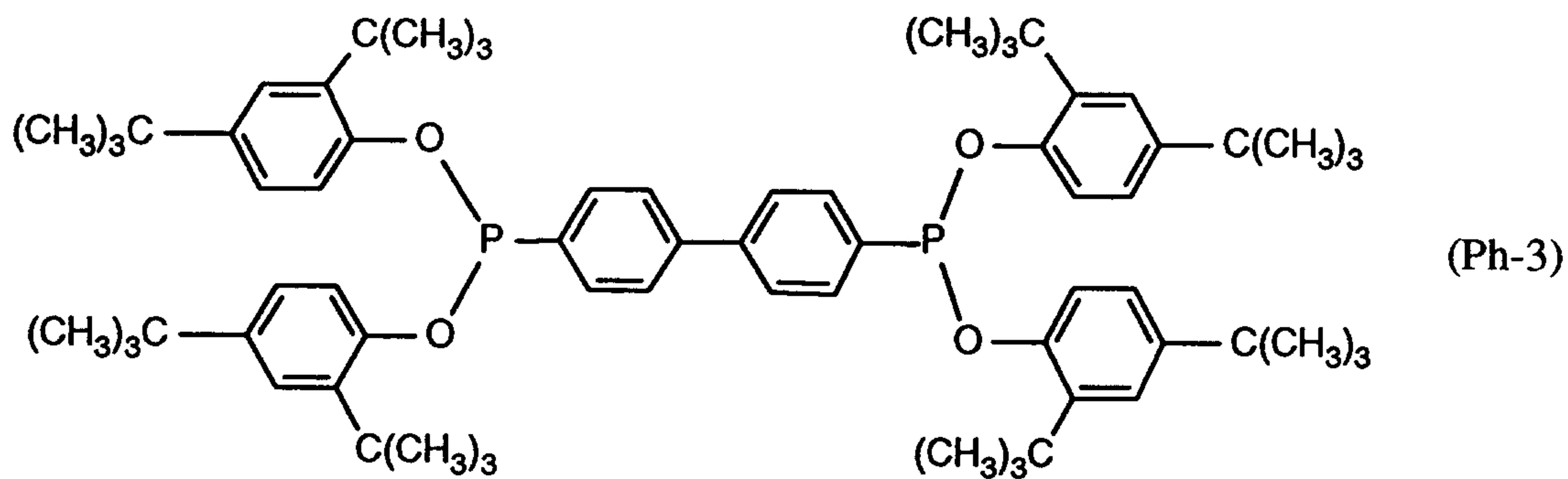
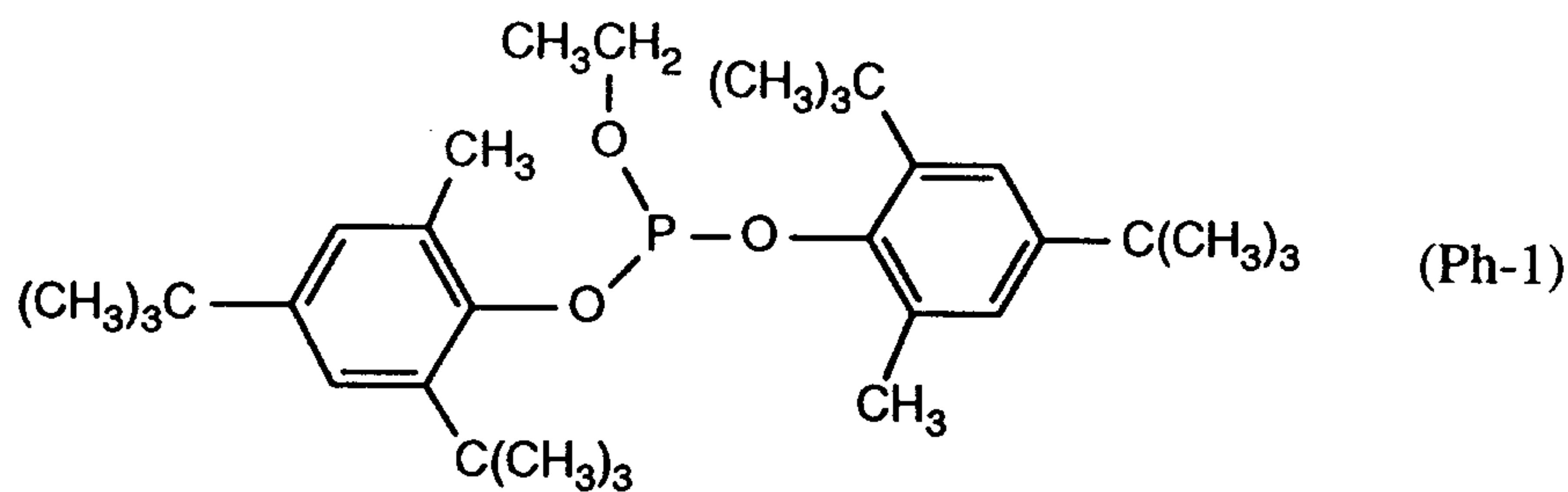


(Ph-11).

These phosphites and phosphonites are known compounds, and some are commercially available.

Particular preference is given to compositions comprising as component (b) a compound of the formula V, Ph-1, Ph-3 or Ph-11





in which

R₉ and R₁₂, independently of one another, are hydrogen, C₁-C₈alkyl, cyclohexyl or phenyl, and

R₁₀ and R₁₁, independently of one another, are hydrogen or C₁-C₄alkyl.

Of interest are compositions comprising as component (c)(i) a compound of the formula I or II in which

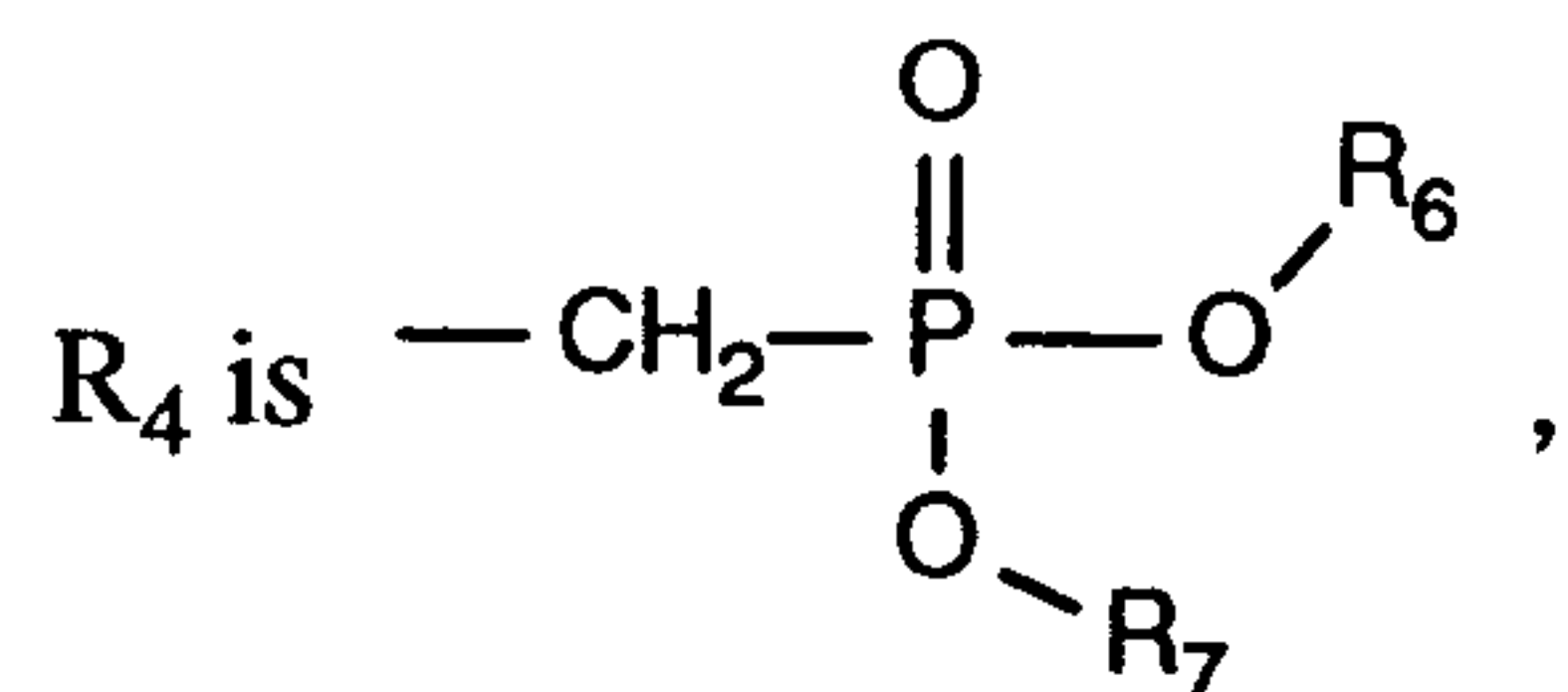
n is the number 1 or 3,

R₁ is C₁-C₁₂alkyl, C₅-C₈cycloalkyl, phenyl or benzyl,

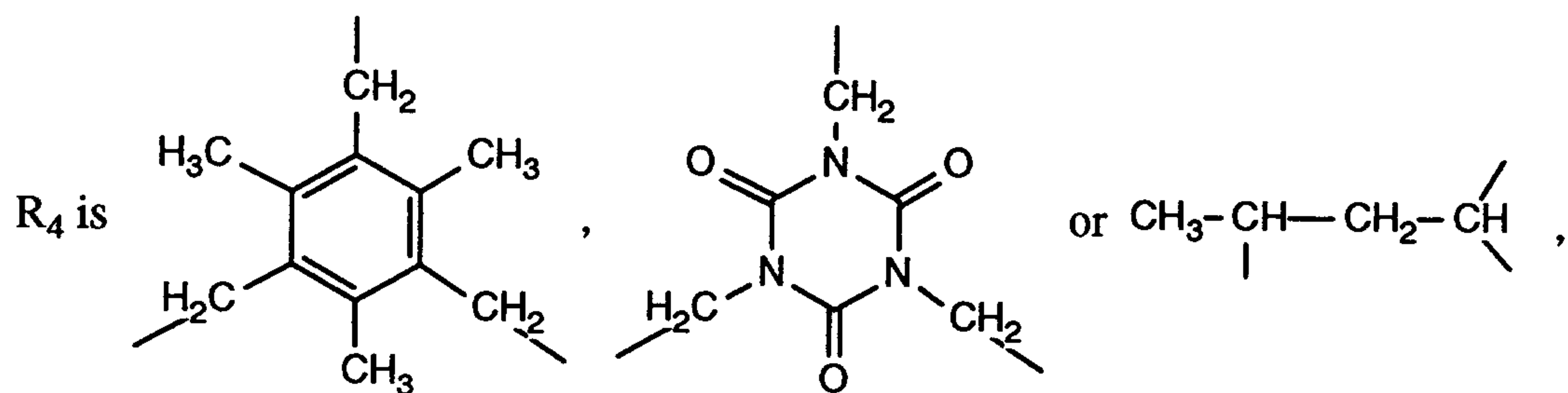
R₂ is hydrogen, C₁-C₁₂alkyl, C₅-C₈cycloalkyl, phenyl or benzyl,

R_3 is hydrogen or methyl,

if n is 1,



if n is 3,



R_5 is hydrogen or methyl,

R_6 is hydrogen, C_1 - C_{12} alkyl or $\frac{M^{r+}}{r}$,

R_7 is C_1 - C_{12} alkyl,

M^{r+} is an r -valent metal cation, and

r is 1, 2 or 3.

Preference is given to compositions comprising as component (c)(i) a compound of the formula I in which

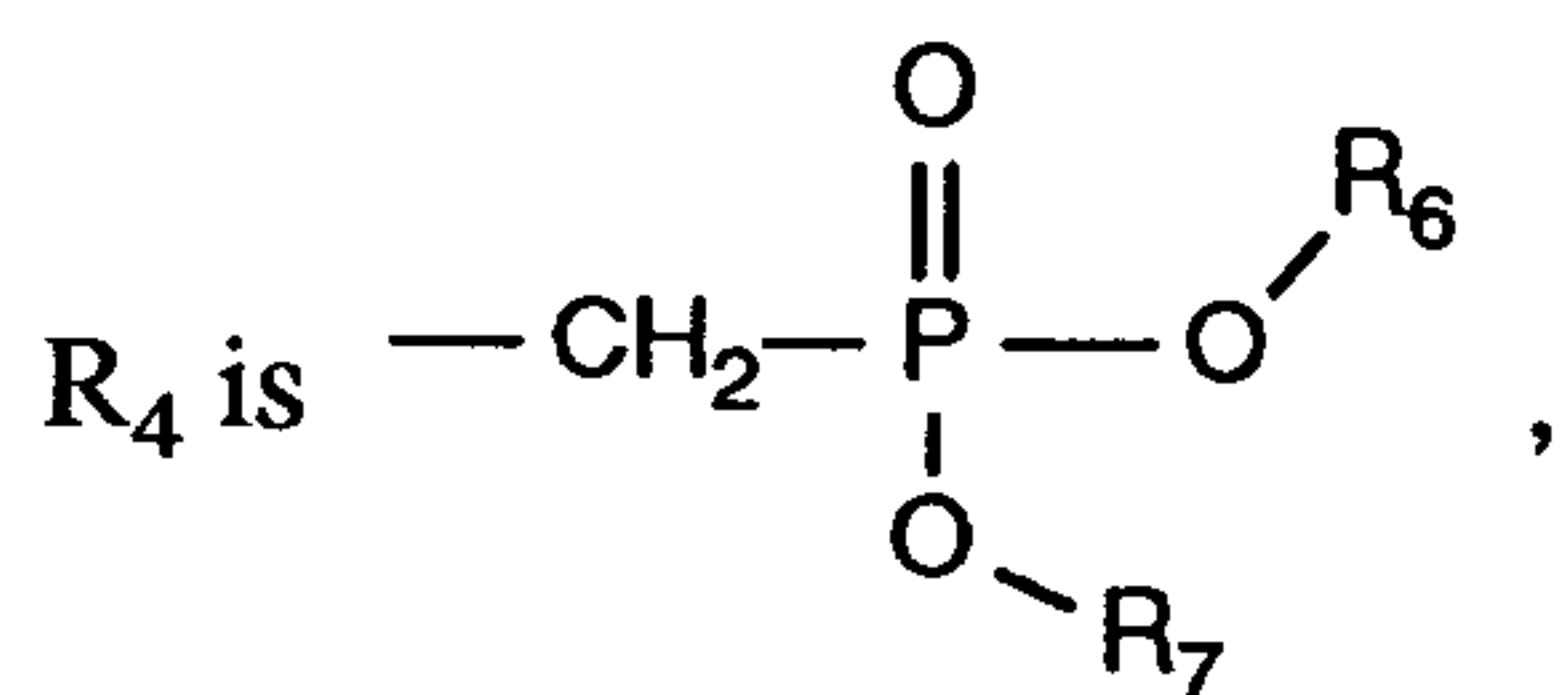
n is the number 1 or 3,

R_1 is tert-butyl, cyclohexyl or phenyl,

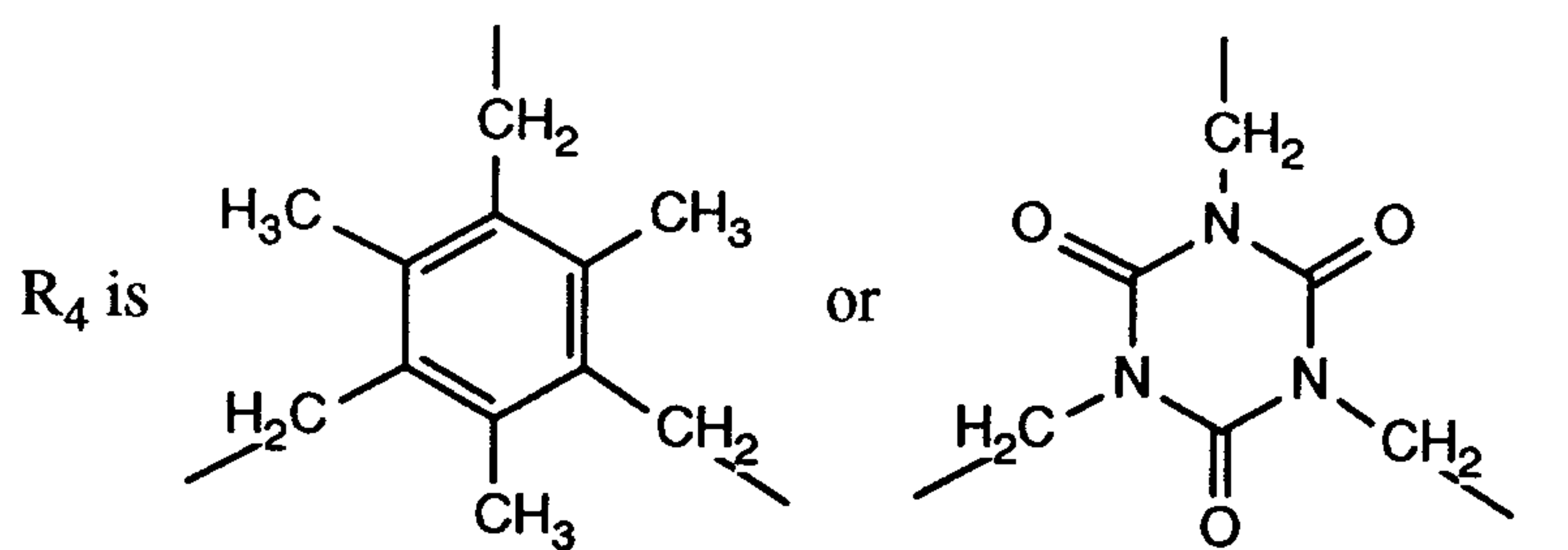
R_2 is hydrogen, tert-butyl, cyclohexyl or phenyl,

R_3 is hydrogen,

if n is 1,



if n is 3,



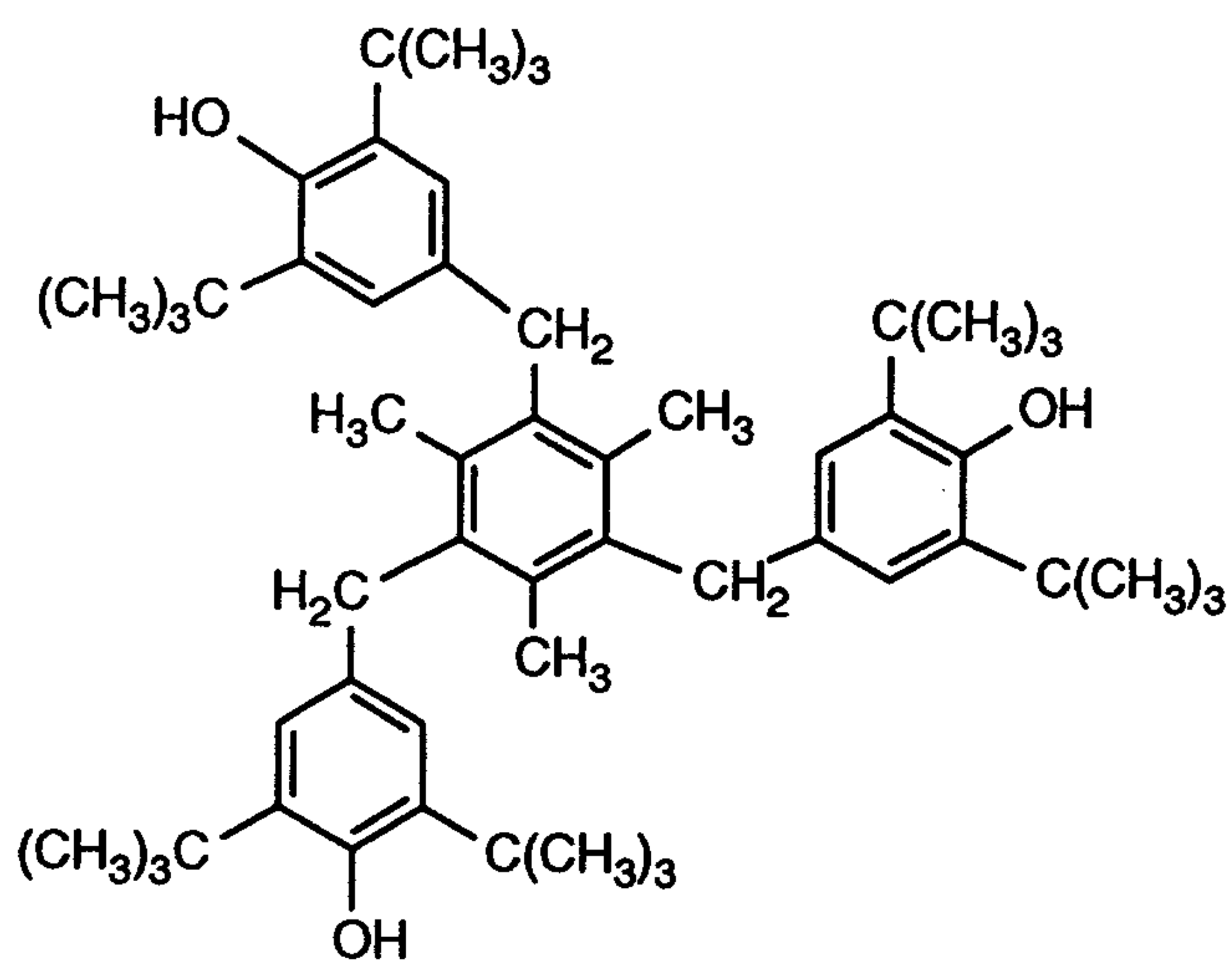
R_6 is C_1 - C_4 alkyl or $\frac{M^{r+}}{r}$,

R_7 is C_1 - C_{12} alkyl,

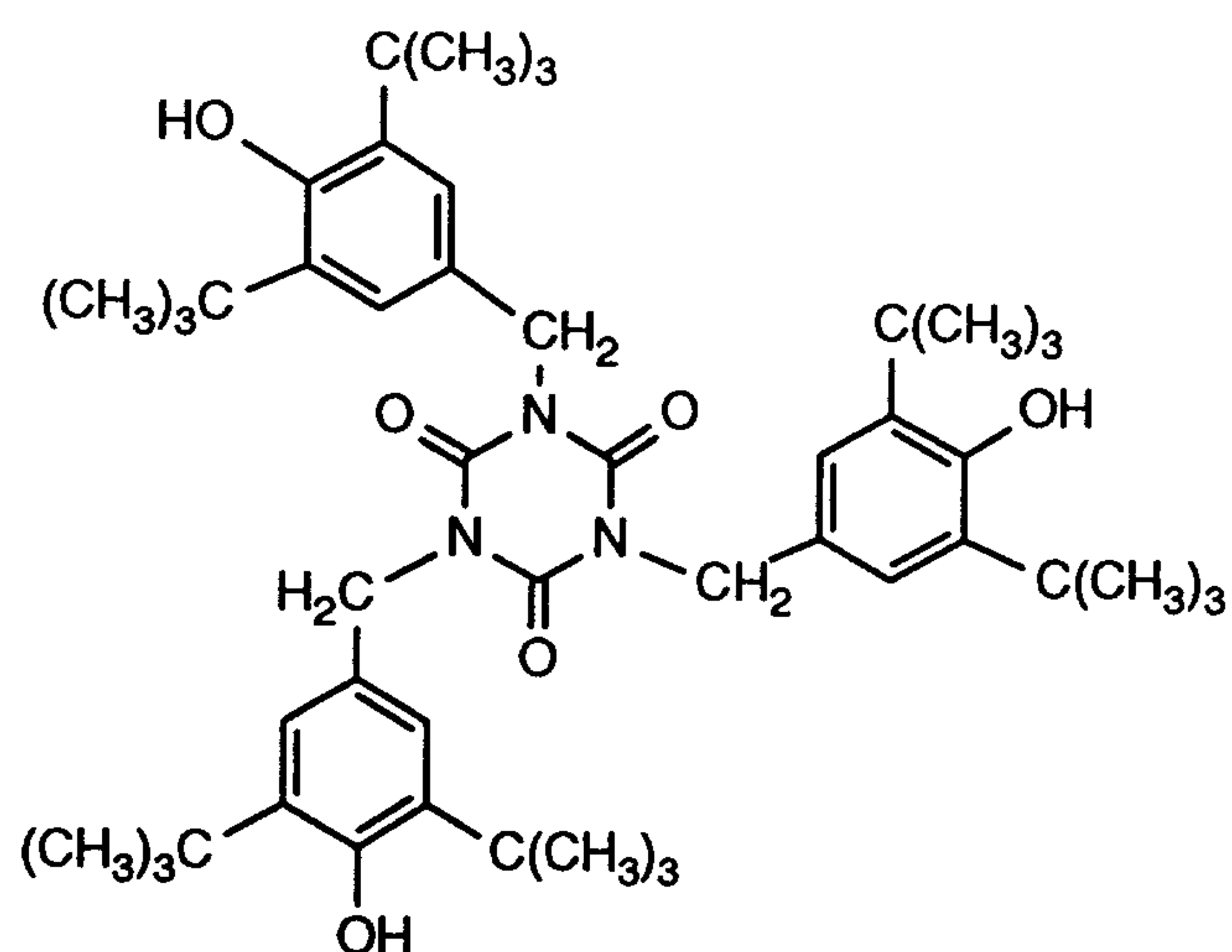
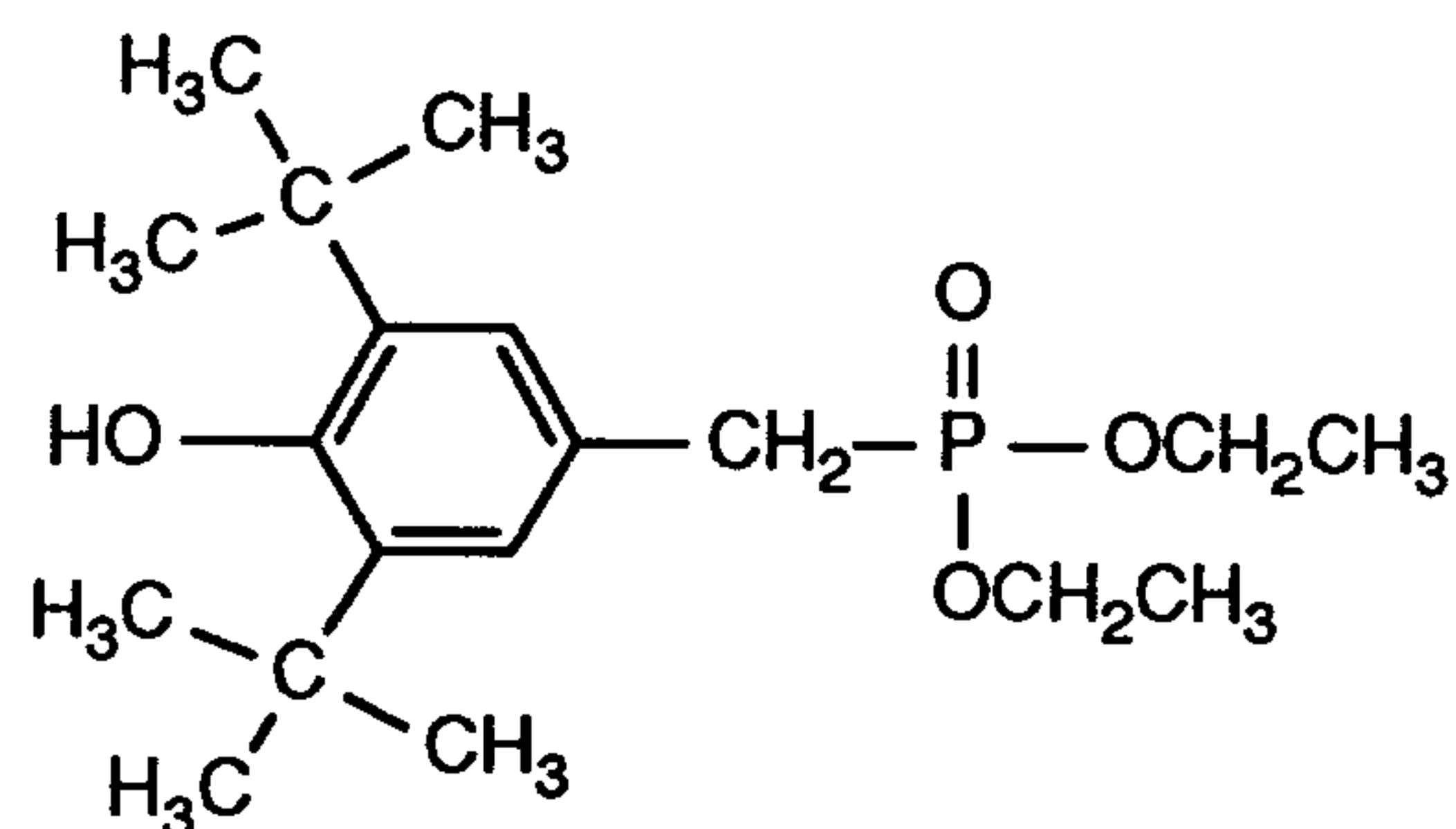
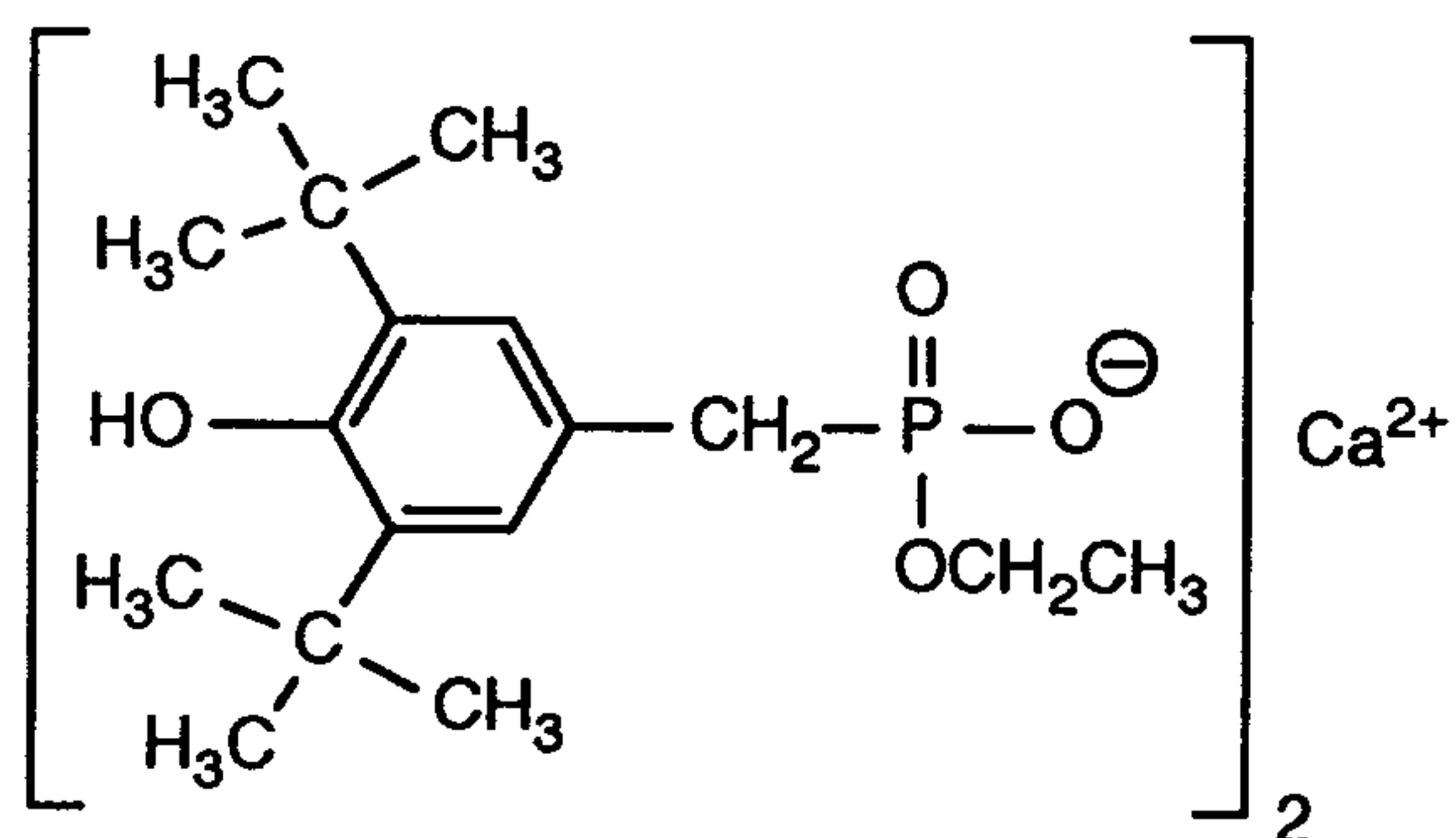
M^{r+} is calcium, and

r is 2.

Very particular preference is given to compositions comprising as component (c)(i) a compound of the formula

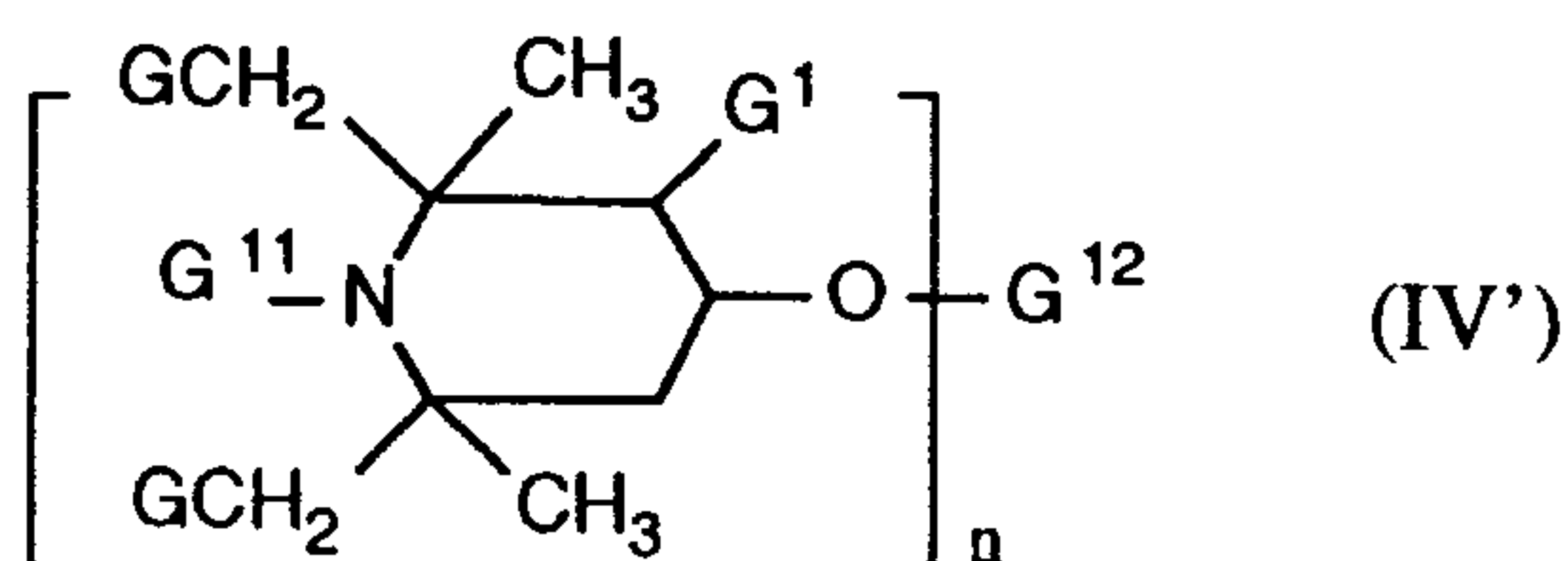


Irganox[®] 1330 (Ciba-Geigy)

Irganox[®] 3114 (Ciba-Geigy)Irganox[®] 1222 (Ciba-Geigy)Irganox[®] 1425 (Ciba-Geigy)

Of particular interest are compositions comprising as component (c)(ii) or component (c)(iii)(y) a sterically hindered amine from the class of compounds described under (a') to (g') which contain at least one radical of the formula III or IV.

(a') Compounds of the formula IV'



in which n is a number from 1 to 4, G and G^1 independently of one another, are hydrogen or methyl,

G^{11} is hydrogen, oxygen, hydroxyl, C_1 - C_{18} alkyl, C_3 - C_8 alkenyl, C_3 - C_8 alkynyl, C_7 - C_{12} aralkyl, C_1 - C_{18} alkoxy, C_5 - C_8 cycloalkoxy, C_7 - C_9 phenylalkoxy, C_1 - C_8 alkanoyl, C_3 - C_5 alkenoyl, C_1 - C_{18} alkanoyloxy, benzyloxy, glycidyl or a group of the formula $-CH_2CH(OH)-Z$, in which Z is hydrogen, methyl or phenyl, G^{11} preferably being H, C_1 - C_4 alkyl, allyl, benzyl, acetyl or acryloyl, and

G^{12} , if n is 1, is hydrogen, C_1 - C_{18} alkyl which is uninterrupted or interrupted by one or more oxygen atoms, cyanoethyl, benzoyl, glycidyl, a monovalent radical or an aliphatic, cycloaliphatic, araliphatic, unsaturated or aromatic carboxylic acid, carbamic acid or phosphorus-containing acid or a monovalent silyl radical, preferably a radical of an aliphatic carboxylic acid having 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid having 7 to 15 carbon atoms, or an α,β -unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms, where each carboxylic acid can be substituted in the aliphatic, cycloaliphatic or aromatic moiety by 1 to 3 $-COOZ^{12}$ groups, in which Z^{12} is H, C_1 - C_{20} alkyl, C_3 - C_{12} alkenyl, C_5 - C_7 cycloalkyl, phenyl or benzyl,

G^{12} , if n is 2, is C_2 - C_{12} alkylene, C_4 - C_{12} alkenylene, xylylene, a divalent radical or an aliphatic, cycloaliphatic, araliphatic or aromatic dicarboxylic acid, dicarbamic acid or phosphorus-containing acid or a divalent silyl radical, preferably a radical of an aliphatic dicarboxylic acid having 2 to 36 carbon atoms, or a cycloaliphatic or aromatic dicarboxylic acid having 8-14 carbon atoms or of an aliphatic, cycloaliphatic or aromatic dicarbamic acid having 8-14 carbon atoms, where each dicarboxylic acid may be substituted in the aliphatic, cycloaliphatic or aromatic moiety by one or two $-COOZ^{12}$ groups,

G^{12} , if n is 3, is a trivalent radical of an aliphatic, cycloaliphatic or aromatic tricarboxylic acid, which may be substituted in the aliphatic, cycloaliphatic or aromatic moiety by $-COOZ^{12}$, of an aromatic tricarbamic acid or of a phosphorus-containing acid, or is a trivalent silyl radical,

and G^{12} , if n is 4, is a tetravalent radical of an aliphatic, cycloaliphatic or aromatic tetracarboxylic acid.

The carboxylic acid radicals mentioned above are in each case taken to mean radicals of the formula $(-CO)_nR$, where n is as defined above, and the meaning of R arises from the definition given.

Any C_1 - C_{12} alkyl substituents are, for example, methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl.

C_1 - C_{18} alkyl G^{11} or G^{12} can be, for example, the abovementioned groups and in addition, for example, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

C_3 - C_8 alkenyl G^{11} can be, for example, 1-propenyl, allyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl, 2-octenyl, or 4-tert-butyl-2-butenyl.

C_3 - C_8 alkynyl G^{11} is preferably propargyl.

C_7 - C_{12} aralkyl G^{11} is, in particular, phenethyl, especially benzyl.

C_1 - C_8 alkanoyl G^{11} is, for example, formyl, propionyl, butyryl, octanoyl, but preferably acetyl and C_3 - C_5 alkenoyl G^{11} is in particular acryloyl.

If G^{12} is a monovalent radical of a carboxylic acid, it is, for example, an acetyl, caproyl, stearoyl, acryloyl, methacryloyl, benzoyl or β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl radical.

If G^{12} is a monovalent silyl radical, it is, for example, a radical of the formula $-(C_jH_{2j})-Si(Z')_2Z''$, in which j is an integer in the range from 2 to 5, and Z' and Z'' , independently of one another, are C_1 - C_4 alkyl or C_1 - C_4 alkoxy.

If G^{12} is a divalent radical of a dicarboxylic acid, it is, for example, a malonyl, succinyl, glutaryl, adipoyl, suberoyl, sebacoyl, maleoyl, itaconyl, phthaloyl, dibutylmalonyl, dibenzylmalonyl, butyl(3,5-di-tert-butyl-4-hydroxybenzyl)malonyl or bicycloheptenedicarbonyl radical.

If G^{12} is a trivalent radical of a tricarboxylic acid, it is, for example, a trimellitoyl, citryl or nitrilotriacetyl radical.

If G^{12} is a tetravalent radical of a tetracarboxylic acid, it is, for example, the tetravalent radical of butane-1,2,3,4-tetracarboxylic acid or of pyromellitic acid.

If G^{12} is a divalent radical of a dicarbamic acid, it is, for example, hexamethylenedicarbamoyl or 2,4-toluylenedicarbamoyl radical.

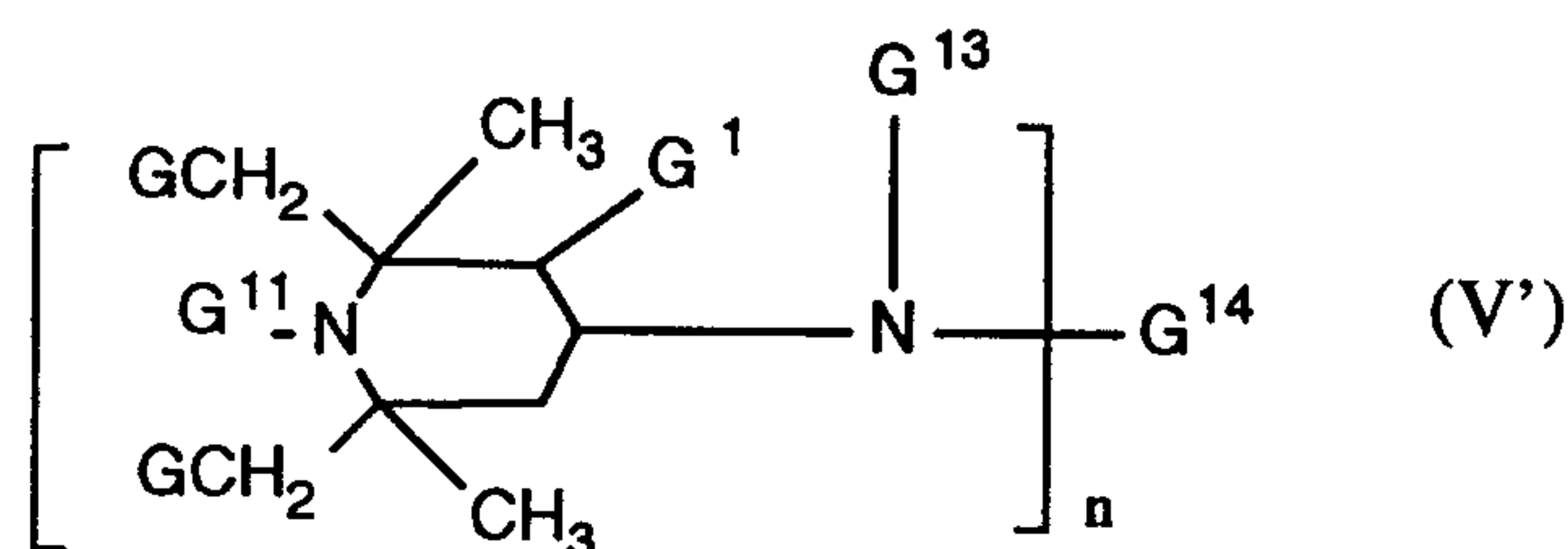
Preference is given to compounds of the formula IV' in which G is hydrogen, G^{11} is hydrogen or methyl, n is 2 and G^{12} is the diacyl radical of an aliphatic dicarboxylic acid having 4-12 carbon atoms.

Examples of polyalkylpiperidine compounds from this class are the following compounds:

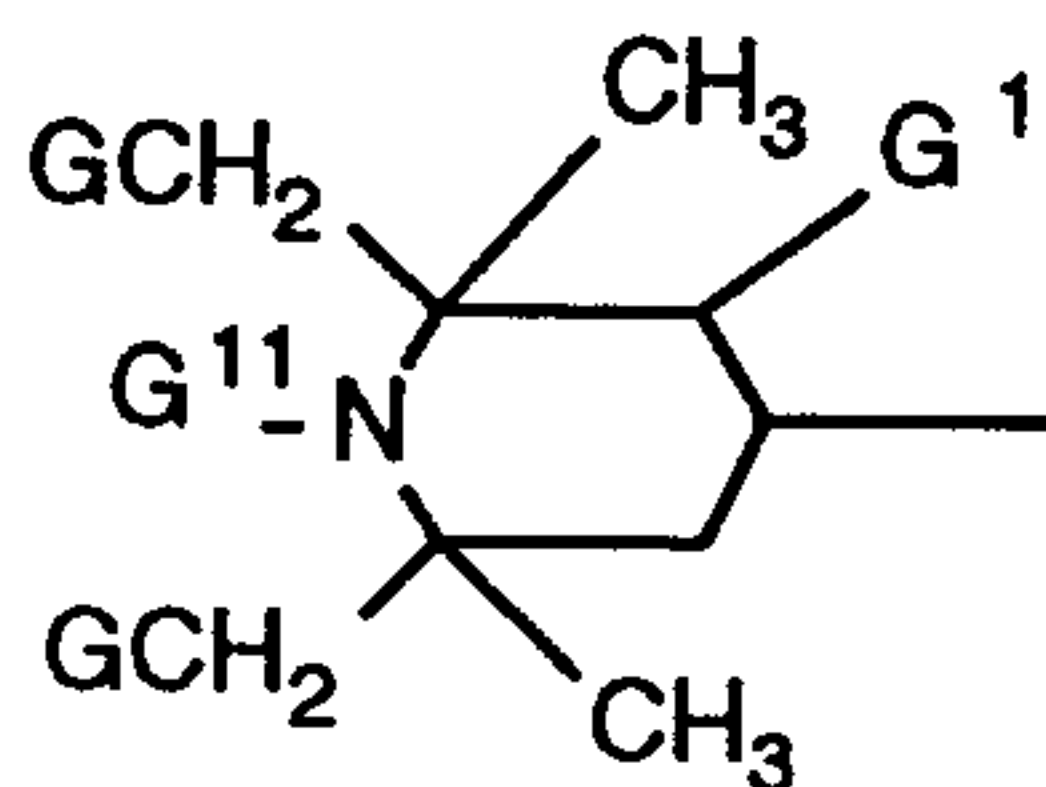
- 1) 4-hydroxy-2,2,6,6-tetramethylpiperidine
- 2) 1-allyl-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 3) 1-benzyl-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 4) 1-(4-tert-butyl-2-butenyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 5) 4-stearoyloxy-2,2,6,6-tetramethylpiperidine
- 6) 1-ethyl-4-salicyloyloxy-2,2,6,6-tetramethylpiperidine
- 7) 4-methacryloyloxy-1,2,2,6,6-pentamethylpiperidine
- 8) 1,2,2,6,6-pentamethylpiperidin-4-yl β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate
- 9) di(1-benzyl-2,2,6,6-tetramethylpiperidin-4-yl) maleate
- 10) di(2,2,6,6-tetramethylpiperidin-4-yl) succinate
- 11) di(2,2,6,6-tetramethylpiperidin-4-yl) glutarate
- 12) di(2,2,6,6-tetramethylpiperidin-4-yl) adipate
- 13) di(2,2,6,6-tetramethylpiperidin-4-yl) sebacate
- 14) di(1,2,2,6,6-pentamethylpiperidin-4-yl) sebacate
- 15) di(1,2,3,6-tetramethyl-2,6-diethyl-piperidin-4-yl) sebacate
- 16) di(1-allyl-2,2,6,6-tetramethylpiperidin-4-yl) phthalate
- 17) 1-hydroxy-4- β -cyanoethoxy-2,2,6,6-tetramethylpiperidine
- 18) 1-acetyl-2,2,6,6-tetramethylpiperidin-4-yl acetate
- 19) tri(2,2,6,6-tetramethylpiperidin-4-yl) trimellitate
- 20) 1-acryloyl-4-benzyloxy-2,2,6,6-tetramethylpiperidine
- 21) di(2,2,6,6-tetramethylpiperidin-4-yl) diethylmalonate
- 22) di(1,2,2,6,6-pentamethylpiperidin-4-yl) dibutylmalonate
- 23) di(1,2,2,6,6-pentamethylpiperidin-4-yl) butyl(3,5-di-tert-butyl-4-hydroxybenzyl)malonate
- 24) di(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate
- 25) di(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate
- 26) hexane-1',6'-bis(4-carbamoyloxy-1-n-butyl-2,2,6,6-tetramethylpiperidine)

- 27) toluene-2',4'-bis-(4-carbamoyloxy-1-n-propyl-2,2,6,6-tetramethylpiperidine)
- 28) dimethylbis(2,2,6,6-tetramethylpiperidin-4-oxy)silane
- 29) phenyltris(2,2,6,6-tetramethylpiperidin-4-oxy)silane
- 30) tris(1-propyl-2,2,6,6-tetramethylpiperidin-4-yl) phosphite
- 31) tris(1-propyl-2,2,6,6-tetramethylpiperidin-4-yl) phosphate
- 32) phenyl bis(1,2,2,6,6-pentamethylpiperidin-4-yl) phosphonate
- 33) 4-hydroxy-1,2,2,6,6-pentamethylpiperidine
- 34) 4-hydroxy-N-hydroxyethyl-2,2,6,6-tetramethylpiperidine
- 35) 4-hydroxy-N-(2-hydroxypropyl)-2,2,6,6-tetramethylpiperidine
- 36) 1-glycidyl-4-hydroxy-2,2,6,6-tetramethylpiperidine

(b') Compounds of the formula V'



in which n is the number 1 or 2, G , G^1 and G^{11} are as defined under (a'), G^{13} is hydrogen, C_1 - C_{12} alkyl, C_2 - C_5 hydroxyalkyl, C_5 - C_7 cycloalkyl, C_7 - C_8 aralkyl, C_2 - C_{18} alkanoyl, C_3 - C_5 alkenoyl, benzoyl or a group of the formula



and

G^{14} , if n is 1, is hydrogen, C_1 - C_{18} alkyl, C_3 - C_8 alkenyl, C_5 - C_7 cycloalkyl, C_1 - C_4 alkyl which is substituted by a hydroxyl, cyano, alkoxycarbonyl or carbamide group, glycidyl, a group of the formula $-\text{CH}_2-\text{CH}(\text{OH})-\text{Z}$ or of the formula $-\text{CONH}-\text{Z}$, in which Z is hydrogen, methyl or phenyl;

G^{14} , if n is 2, is C_2 - C_{12} alkylene, C_6 - C_{12} arylene, xylylene, a $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2$ group or a $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-\text{D}-\text{O}-$ group, in which D is C_2 - C_{10} alkylene, C_6 - C_{15} arylene, C_6 - C_{12} cycloalkylene, or, provided that G^{13} is not alkanoyl, alkenoyl or benzoyl, G^{14} can

alternatively be 1-oxo-C₂-C₁₂alkylene, a divalent radical of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid or dicarbamic acid or alternatively the group -CO-, or, if n is 1, G¹³ and G¹⁴ together can be the divalent radical of an aliphatic, cycloaliphatic or aromatic 1,2- or 1,3-dicarboxylic acid.

Any C₁-C₁₂- or C₁-C₁₈alkyl substituents are as defined above for (a').

Any C₅-C₇cycloalkyl substituents are, in particular, cyclohexyl.

C₇-C₈aralkyl G¹³ is, in particular, phenylethyl or especially benzyl. C₂-C₅Hydroxyalkyl G¹³ is, in particular, 2-hydroxyethyl or 2-hydroxypropyl.

C₂-C₁₈alkanoyl G¹³ is, for example, propionyl, butyryl, octanoyl, dodecanoyl, hexadecanoyl, octadecanoyl, but preferably acetyl, and C₃-C₅alkenoyl G¹³ is, in particular, acryloyl.

C₂-C₈alkenyl G¹⁴ is, for example, allyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl or 2-octenyl.

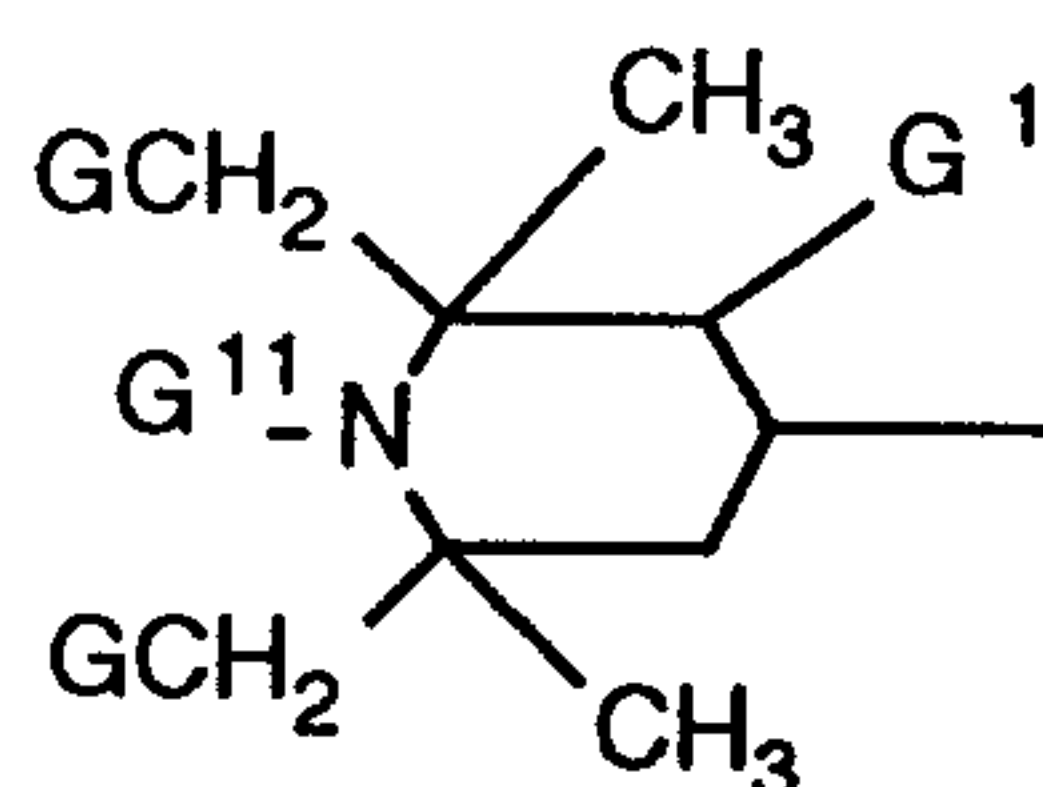
G¹⁴ as a hydroxyl-, cyano-, alkoxycarbonyl- or carbamide-substituted C₁-C₄alkyl can be, for example, 2-hydroxyethyl, 2-hydroxypropyl, 2-cyanoethyl, methoxycarbonylmethyl, 2-ethoxycarbonylethyl, 2-aminocarbonylpropyl or 2-(dimethylaminocarbonyl)ethyl.

Any C₂-C₁₂alkylene substitutes are, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

Any C₆-C₁₅arylene substituents are, for example, o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

C₆-C₁₂cycloalkylene is, in particular cyclohexylene.

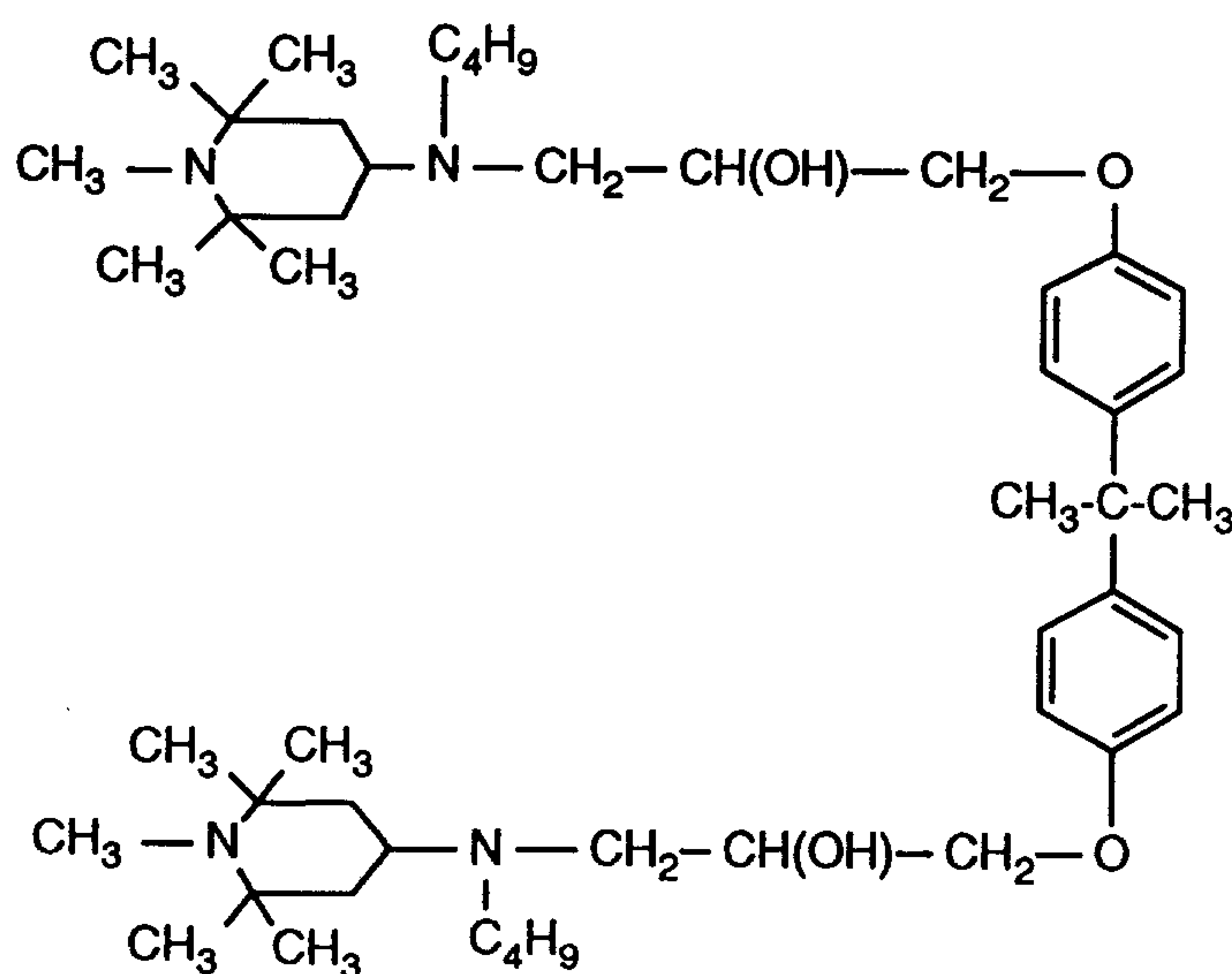
Preference is given to compounds of the formula V' in which n is 1 or 2, G is hydrogen, G¹¹ is hydrogen or methyl, G¹³ is hydrogen, C₁-C₁₂alkyl or a group of the formula



and G^{14} , in the case where $n=1$, is hydrogen or C_1 - C_{12} alkyl, and, in the case where $n=2$, is C_2 - C_8 alkylene or 1-oxo- C_2 - C_8 alkylene.

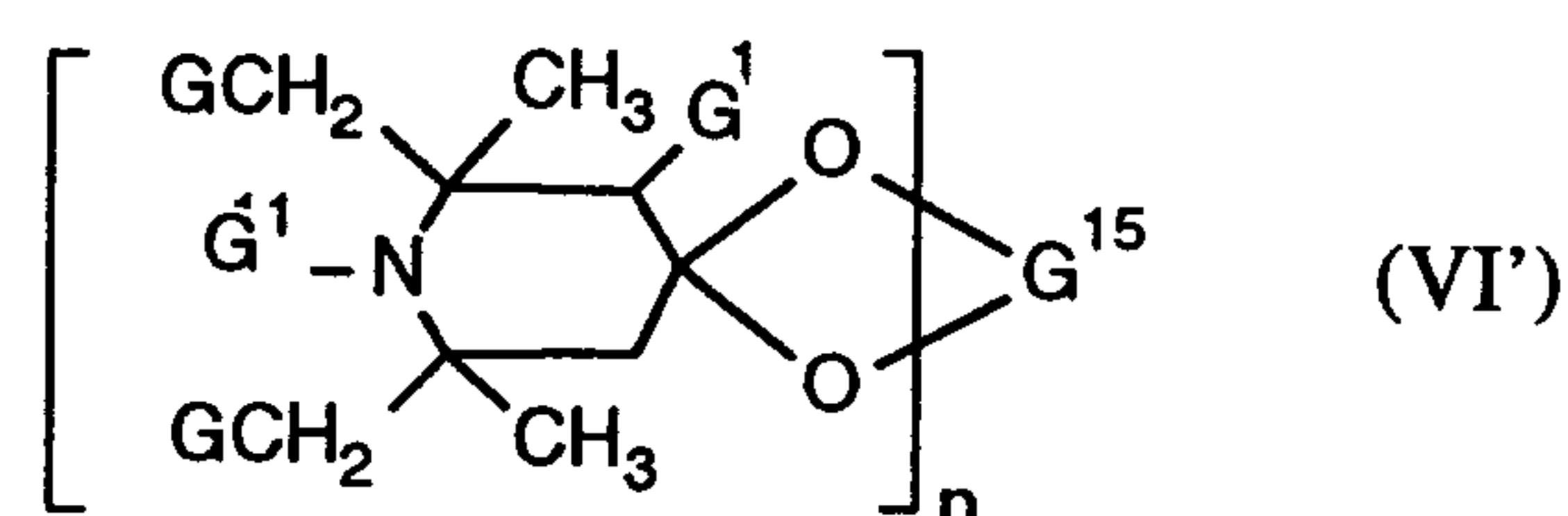
Examples of polyalkylpiperidine compounds from this class are the following compounds:

- 37) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylene-1,6-diamine
- 38) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylene-1,6-diacetamide
- 39) bis(2,2,6,6-tetramethylpiperidin-4-yl)amine
- 40) 4-benzoylamino-2,2,6,6-tetramethylpiperidine
- 41) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)-N,N'-dibutyladipamide
- 42) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)-N,N'-dicyclohexyl-2-hydroxypropylene-1,3-diamine
- 43) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)-p-xylylenediamine
- 44) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)succinamide
- 45) di(2,2,6,6-tetramethylpiperidin-4-yl) N-(2,2,6,6-tetramethylpiperidin-4-yl)- β -aminodipropionate
- 46) The compound of the formula



- 47) 4-(bis-2-hydroxyethylamino)-1,2,2,6,6-pentamethylpiperidine
 48) 4-(3-methyl-4-hydroxy-5-tert-butyl-benzamido)-2,2,6,6-tetramethylpiperidine
 49) 4-methacrylamido-1,2,2,6,6-pentamethylpiperidine

(c') Compounds of the formula VI'



in which n is the number 1 or 2, G , G^1 and G^{11} are as defined under (a), and G^{15} , if n is 1, is C_2 - C_8 alkylene, or C_2 - C_8 hydroxyalkylene or C_4 - C_{22} acyloxyalkylene, and if n is 2, G^{15} is the $(-\text{CH}_2)_2\text{C}(\text{CH}_2-)_2$ group.

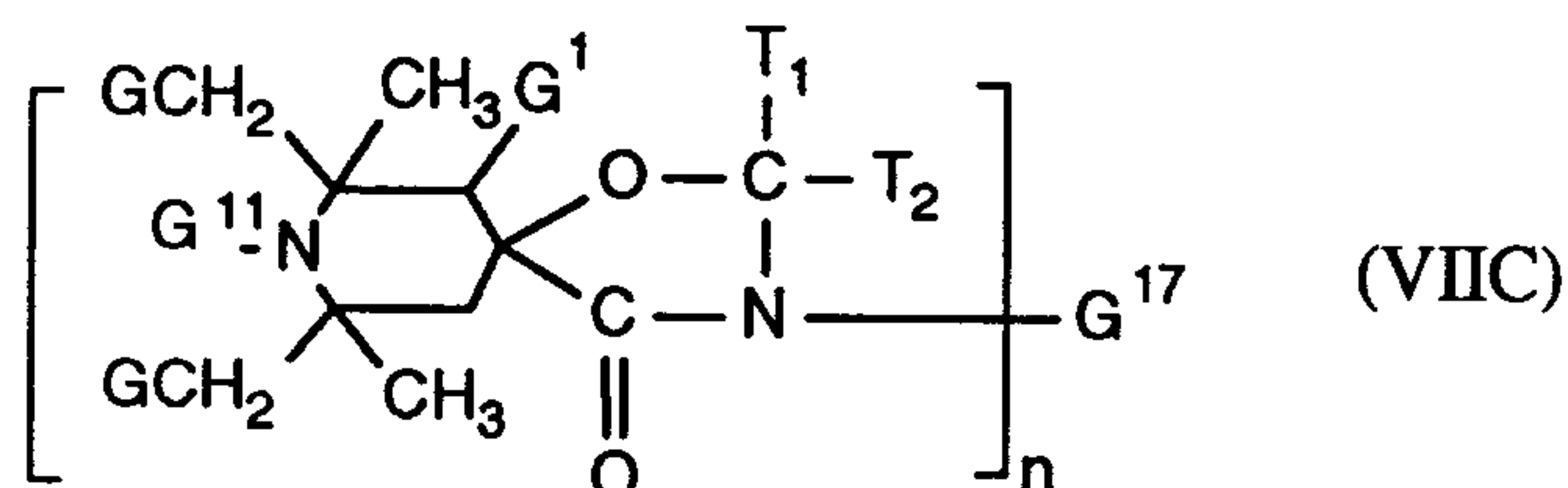
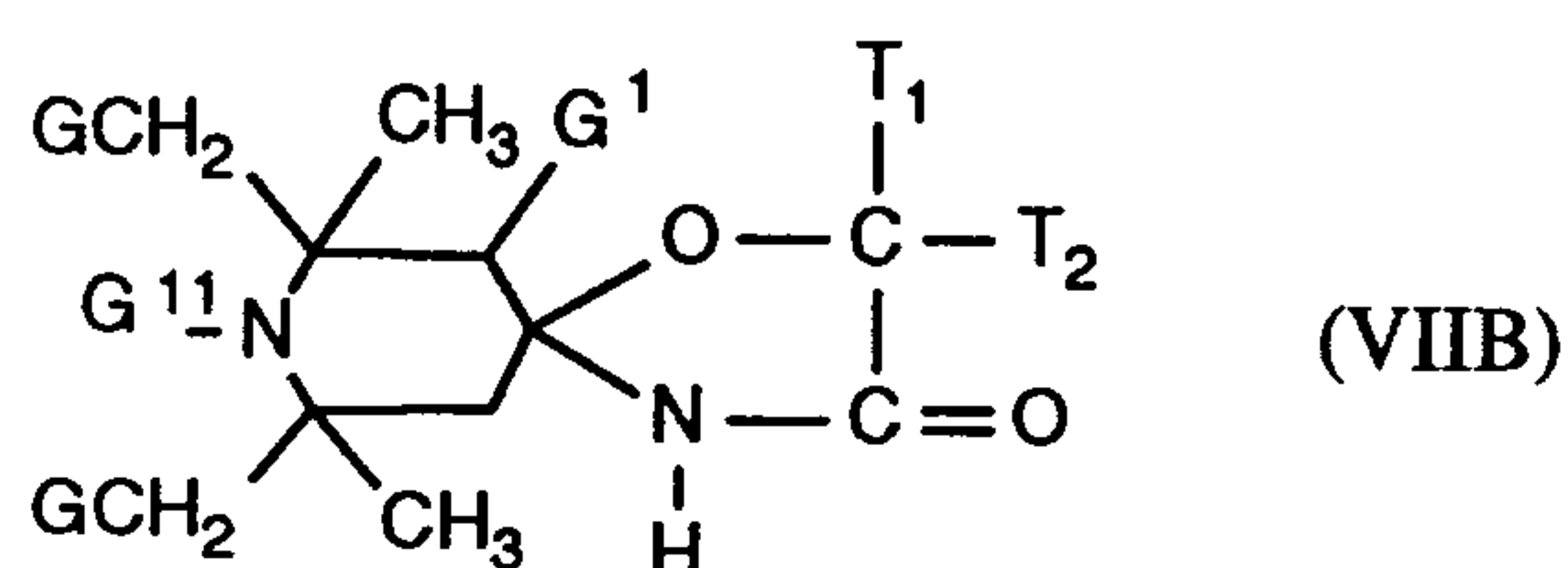
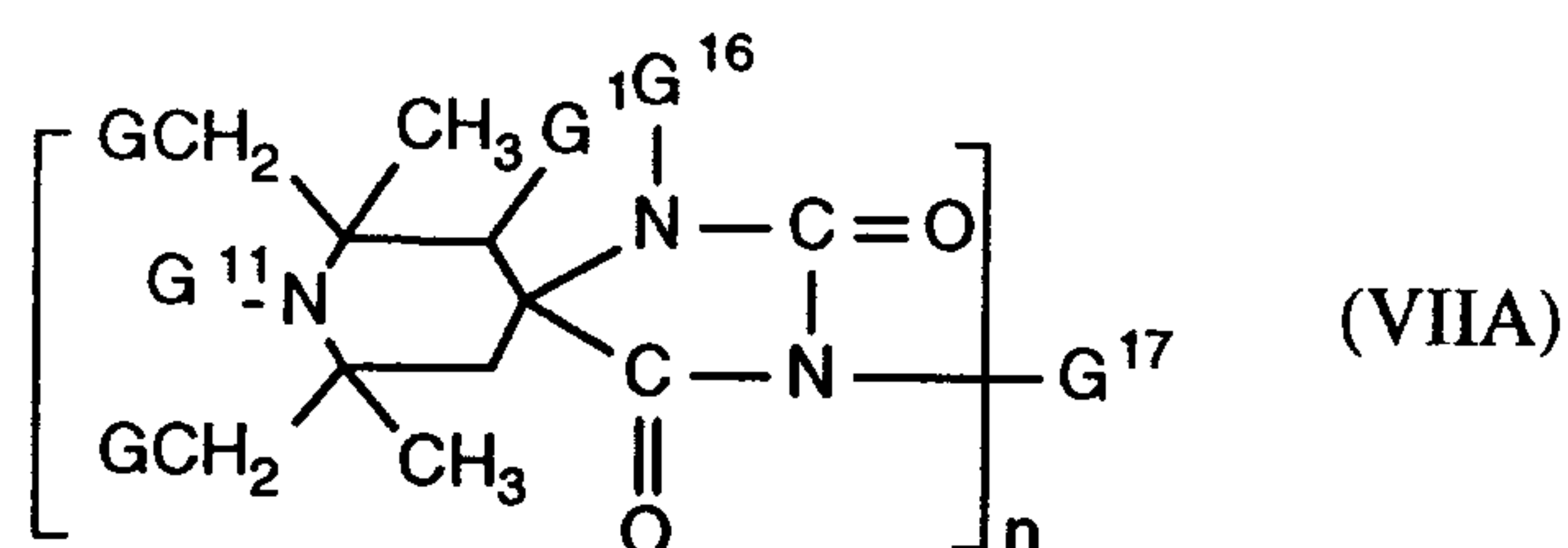
C_2 - C_8 alkylene or C_2 - C_8 hydroxyalkylene G^{15} is, for example, ethylene, 1-methylethylene, propylene, 2-ethylpropylene or 2-ethyl-2-hydroxymethylpropylene.

C_4 - C_{22} acyloxyalkylene G^{15} is, for example, 2-ethyl-2-acetoxymethylpropylene.

Examples of polyalkylpiperidine compounds from this class are the following compounds:

- 50) 9-aza-8,8,10,10-tetramethyl-1,5-dioxaspiro[5.5]undecane
 51) 9-aza-8,8,10,10-tetramethyl-3-ethyl-1,5-dioxaspiro[5.5]undecane
 52) 8-aza-2,7,7,8,9,9-hexamethyl-1,4-dioxaspiro[4.5]decane
 53) 9-aza-3-hydroxymethyl-3-ethyl-8,8,9,10,10-pentamethyl-1,5-dioxaspiro[5.5]undecane
 54) 9-aza-3-ethyl-3-acetoxymethyl-9-acetyl-8,8,10,10-tetramethyl-1,5-dioxaspiro[5.5]-undecane
 55) 2,2,6,6-tetramethylpiperidine-4-spiro-2'-(1',3'-dioxane)-5'-spiro-5''-(1'',3''-dioxane)-2''-spiro-4'''-(2''',2''',6''',6'''-tetramethylpiperidine);

(d') Compounds of the formulae VIIA, VIIB and VIIC, preference being given to compounds of the formula VIIC,



in which n is the number 1 or 2, G , G^1 and G^{11} are as defined under (a'), G^{16} is hydrogen, C_1 - C_{12} alkyl, allyl, benzyl, glycidyl or C_2 - C_6 alkoxyalkyl, and G^{17} , if n is 1, is hydrogen, C_1 - C_{12} alkyl, C_3 - C_5 alkenyl, C_7 - C_9 aralkyl, C_5 - C_7 cycloalkyl, C_2 - C_4 hydroxyalkyl, C_2 - C_6 alkoxyalkyl, C_6 - C_{10} aryl, glycidyl or a group of the formula $-(CH_2)_p\text{-COO-Q}$ or of the formula $-(CH_2)_p\text{-O-CO-Q}$, in which p is 1 or 2, and Q is C_1 - C_4 alkyl or phenyl, and G^{17} , if n is 2, is C_2 - C_{12} alkylene, C_4 - C_{12} alkenylene, C_6 - C_{12} arylene, a group of the formula $-\text{CH}_2\text{-CH(OH)-CH}_2\text{-O-D-O-CH}_2\text{-CH(OH)-CH}_2-$, in which D is C_2 - C_{10} alkylene, C_6 - C_{15} arylene, C_6 - C_{12} cycloalkylene or a group of the formula $-\text{CH}_2\text{CH(OZ')CH}_2\text{-(OCH}_2\text{-CH(OZ')CH}_2\text{)}_2-$, in which Z' is hydrogen, C_1 - C_{18} alkyl, allyl, benzyl, C_2 - C_{12} alkanoyl or benzoyl, T_1 and T_2 , independently of one another, are hydrogen, C_1 - C_{18} alkyl or unsubstituted or halogen- or C_1 - C_4 alkyl-substituted C_6 - C_{10} aryl or C_7 - C_9 aralkyl, or T_1 and T_2 together with the carbon atom bonding them form a C_5 - C_{14} cycloalkane ring.

Any C_1 - C_{12} alkyl substituents are, for example, methyl, ethyl, *n*-propyl, *n*-butyl, *sec*-butyl, *tert*-butyl, *n*-hexyl, *n*-octyl, 2-ethylhexyl, *n*-nonyl, *n*-decyl, *n*-undecyl or *n*-dodecyl.

Any C_1 - C_{18} alkyl substituents can be, for example, the abovementioned groups and in addition, for example, *n*-tridecyl, *n*-tetradecyl, *n*-hexadecyl or *n*-octadecyl.

Any C₂-C₆alkoxyalkyl substituents are, for example, methoxymethyl, ethoxymethyl, propoxymethyl, tert-butoxymethyl, ethoxyethyl, ethoxypropyl, n-butoxyethyl, tert-butoxyethyl, isopropoxyethyl or propoxypropyl.

C₃-C₅alkenyl G¹⁷ is, for example, 1-propenyl, allyl, methallyl, 2-butenyl or 2-pentenyl.

C₇-C₉aralkyl G¹⁷, T₁ and T₂ are, in particular, phenethyl or especially benzyl. If T₁ and T₂ together with the carbon atom form a cycloalkane ring, this can be, for example, a cyclopentane, cyclohexane, cyclooctane or cyclododecane ring.

C₂-C₄hydroxyalkyl G¹⁷ is, for example, 2-hydroxyethyl, 2-hydroxypropyl, 2-hydroxybutyl or 4-hydroxybutyl.

C₆-C₁₀aryl G¹⁷, T₁ and T₂ are, in particular, phenyl or α- or β-naphthyl, which are unsubstituted or substituted by halogen or C₁-C₄alkyl.

C₂-C₁₂alkylene G¹⁷ is, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

C₄-C₁₂alkenylene G¹⁷ is, in particular, 2-butenylene, 2-pentenylene or 3-hexenylene.

C₆-C₁₂arylene G¹⁷ is, for example, o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

C₂-C₁₂alkanoyl Z' is, for example, propionyl, butyryl, octanoyl, dodecanoyl, but preferably acetyl.

C₂-C₁₀alkylene, C₆-C₁₅arylene or C₆-C₁₂cycloalkylene D is as defined under (b').

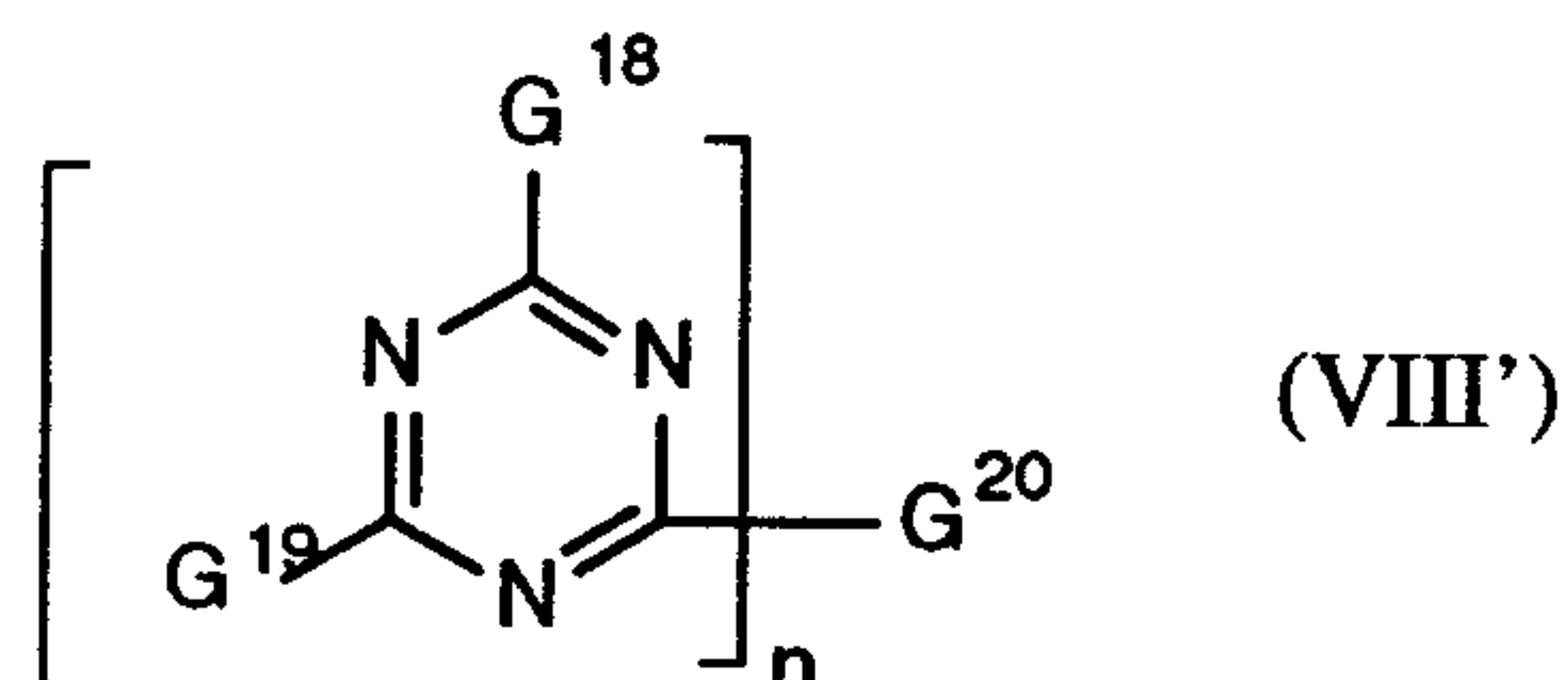
Examples of polyalkylpiperidine compounds from this class are the following compounds:

- 56) 3-benzyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]decane-2,4-dione
- 57) 3-n-octyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]decane-2,4-dione
- 58) 3-allyl-1,3,8-triaza-1,7,7,9,9-pentamethylspiro[4.5]decane-2,4-dione
- 59) 3-glycidyl-1,3,8-triaza-7,7,8,9,9-pentamethylspiro[4.5]decane-2,4-dione
- 60) 1,3,7,7,8,9,9-heptamethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione

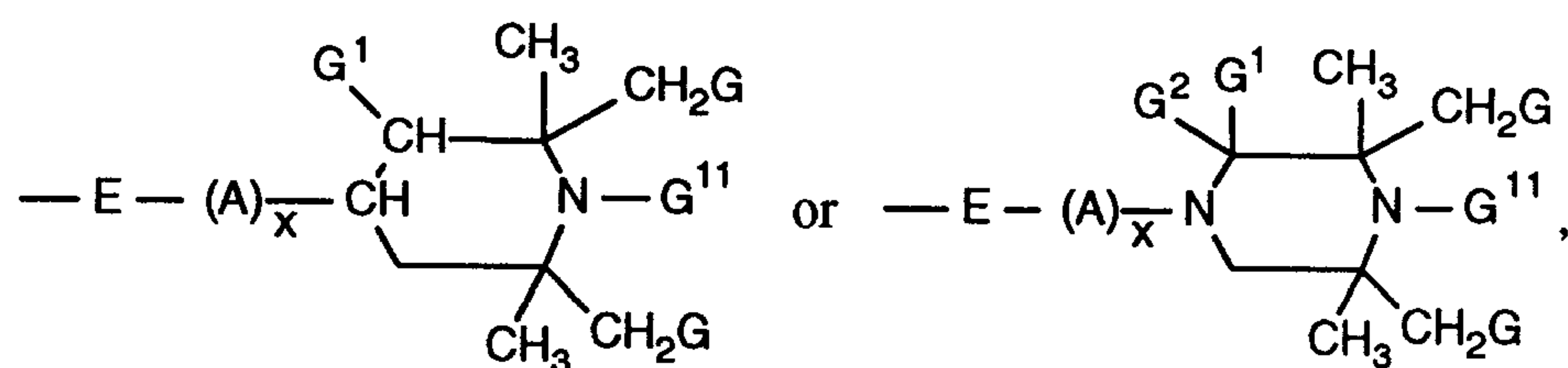
- 61) 2-isopropyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decane
- 62) 2,2-dibutyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decane
- 63) 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-21-oxodispiro[5.1.11.2]heneicosane
- 64) 2-butyl-7,7,9,9-tetramethyl-1-oxa-4,8-diaza-3-oxospiro[4.5]decane and preferably:
- 65) 8-acetyl-3-dodecyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]decane-2,4-dione

and the compounds of the following formulae:

(e') Compounds of the formula VIII', which are themselves preferred,



in which n is the number 1 or 2, and G¹⁸ is a group of the formula



in which G and G¹¹ are as defined under (a'), and G¹ and G² are hydrogen, methyl or, together, are a substituent =O,

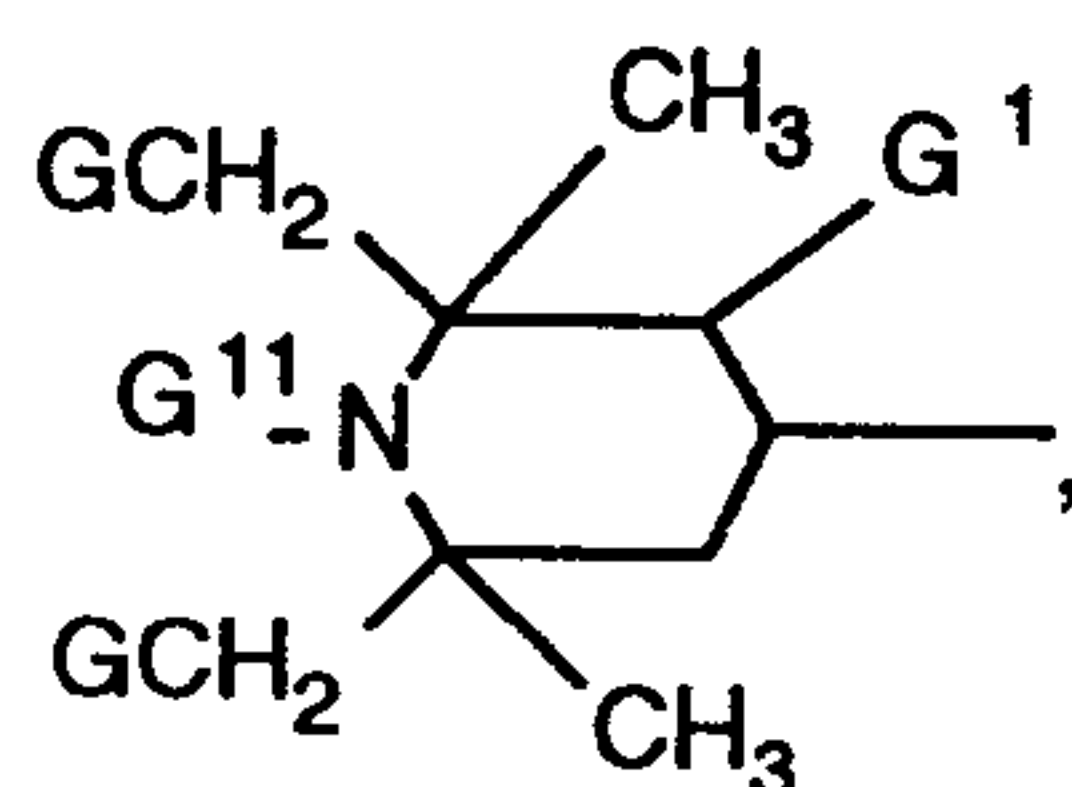
E is -O- or -NG¹³-, A is C₂-C₆alkylene or -(CH₂)₃-O- and x is the number 0 or 1,

G¹³ is hydrogen, C₁-C₁₂alkyl, C₂-C₅hydroxyalkyl or C₅-C₇cycloalkyl,

G¹⁹ is identical to G¹⁸ or is one of the groups -NG²¹G²², -OG²³, -NHCH₂OG²³ or -N(CH₂OG²³)₂,

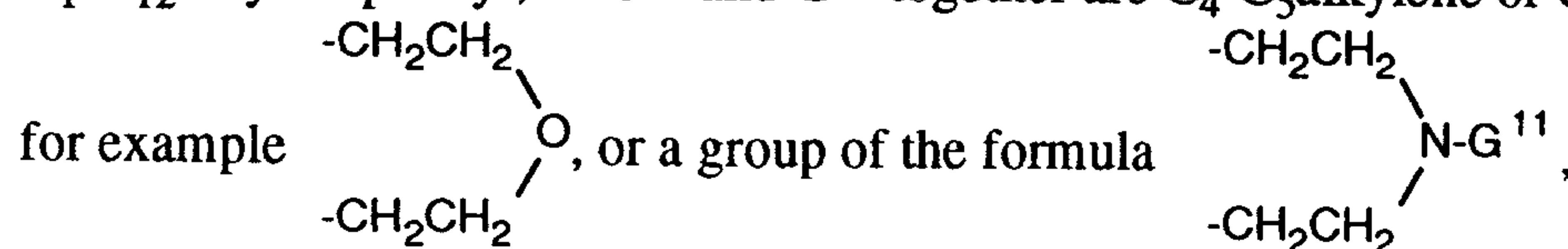
G²⁰, if n = 1, is identical to G¹⁸ or G¹⁹ and, if n = 2, is an -E-B-E- group, in which B is C₂-C₈alkylene or C₂-C₈alkylene which is interrupted by 1 or 2 -N(G²¹)- groups,

G²¹ is C₁-C₁₂alkyl, cyclohexyl, benzyl or C₁-C₄-hydroxyalkyl or a group of the formula

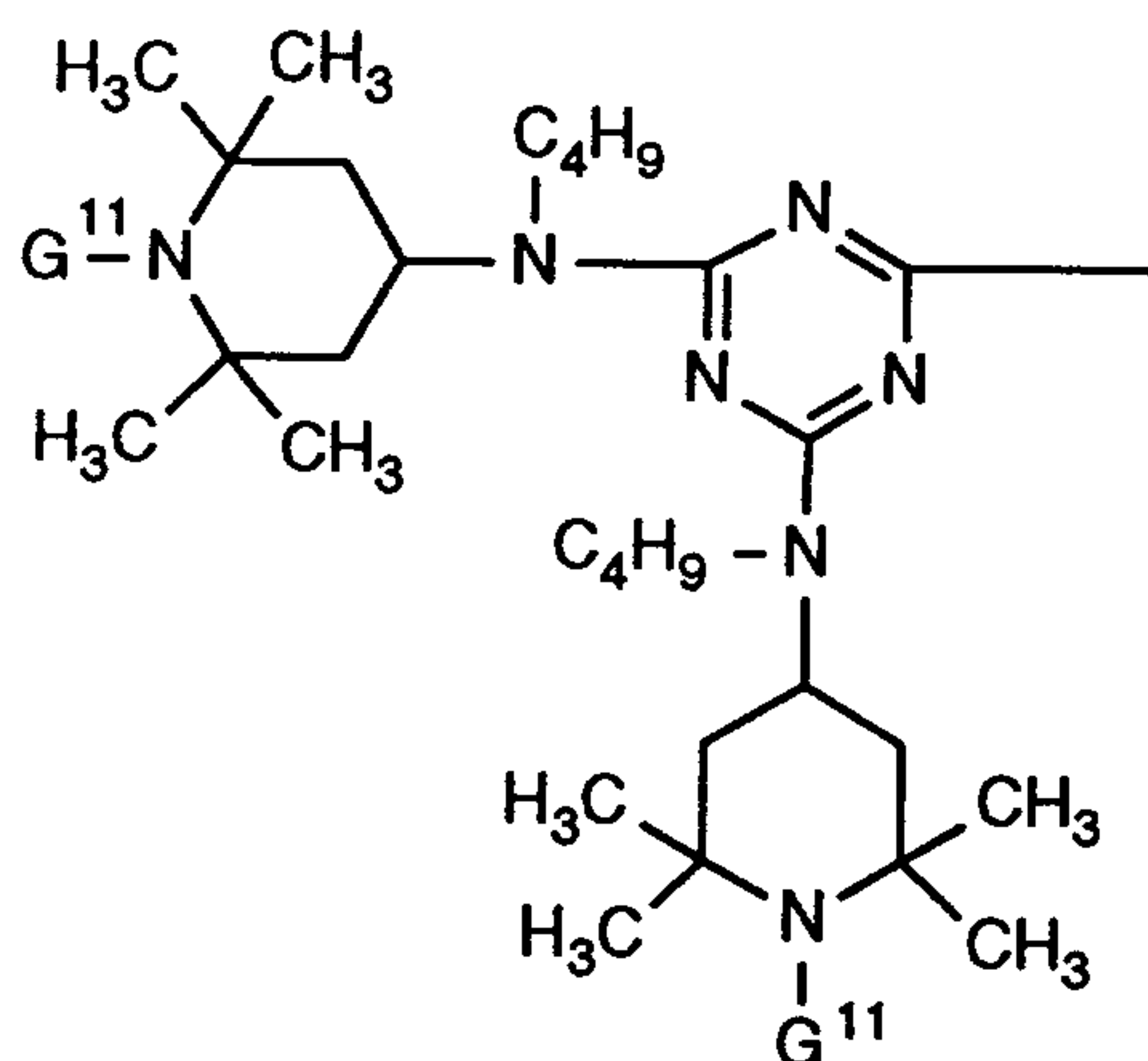


G²² is C₁-C₁₂alkyl, cyclohexyl, benzyl or C₁-C₄hydroxyalkyl, and G²³ is hydrogen,

C₁-C₁₂alkyl or phenyl, or G²¹ and G²² together are C₄-C₅alkylene or C₄-C₅oxaalkylene,



or G^{21} is a group of the formula



Any C_1 - C_{12} alkyl substituents are, for example, methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl.

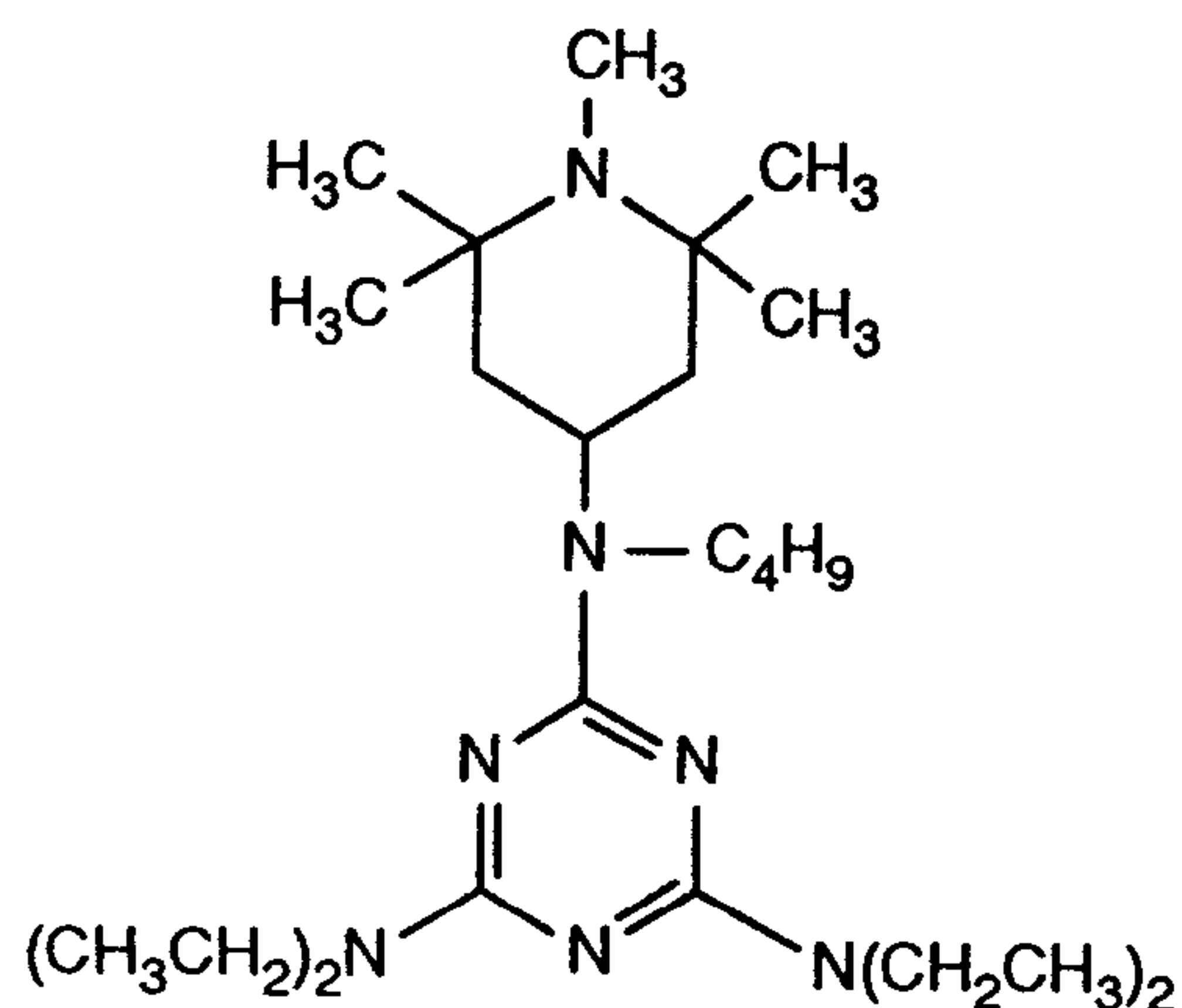
Any C_1 - C_4 hydroxyalkyl substituents are, for example, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 2-hydroxybutyl or 4-hydroxybutyl.

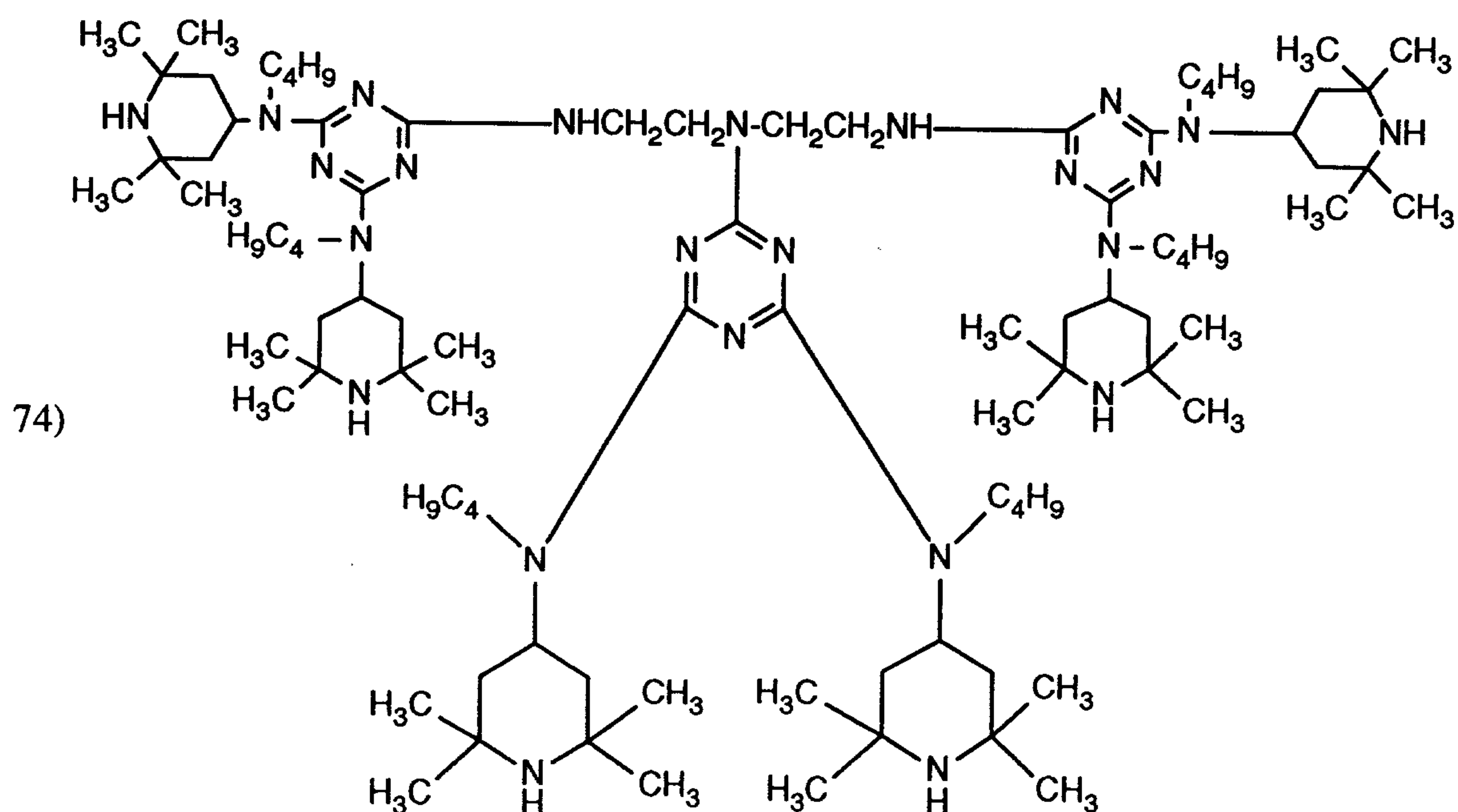
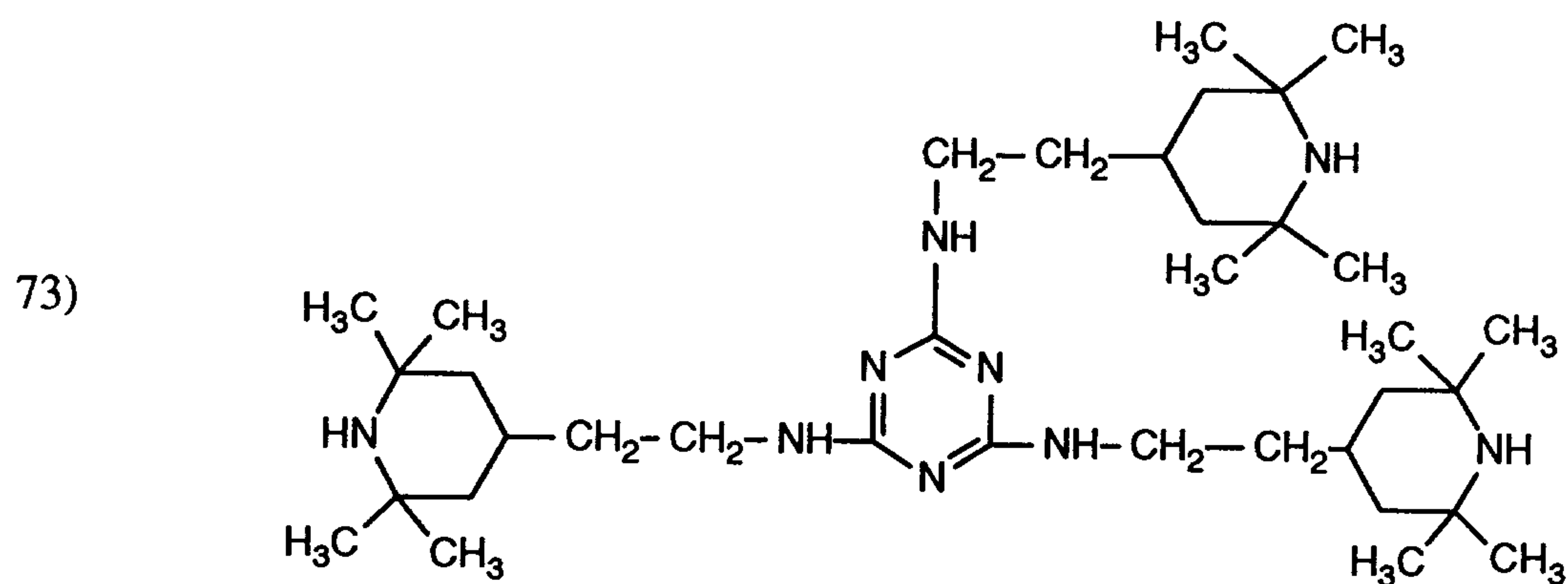
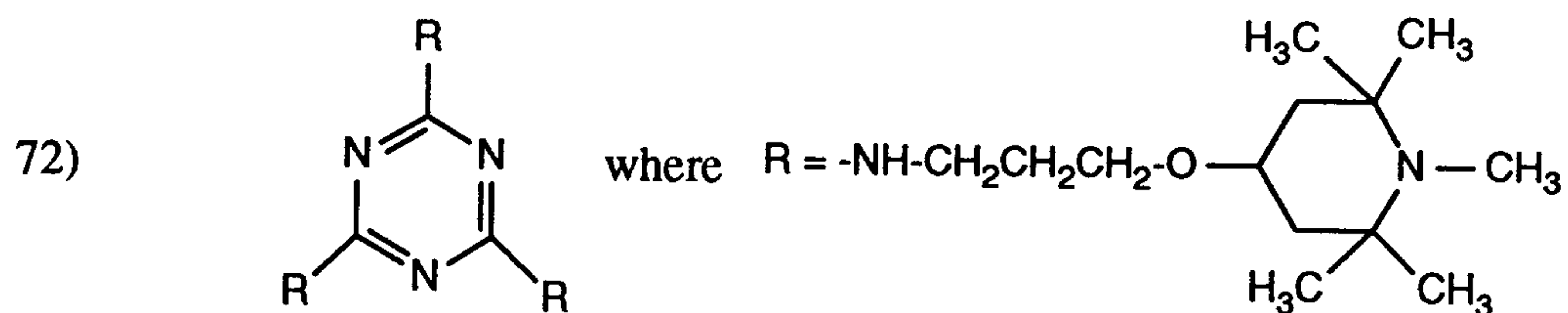
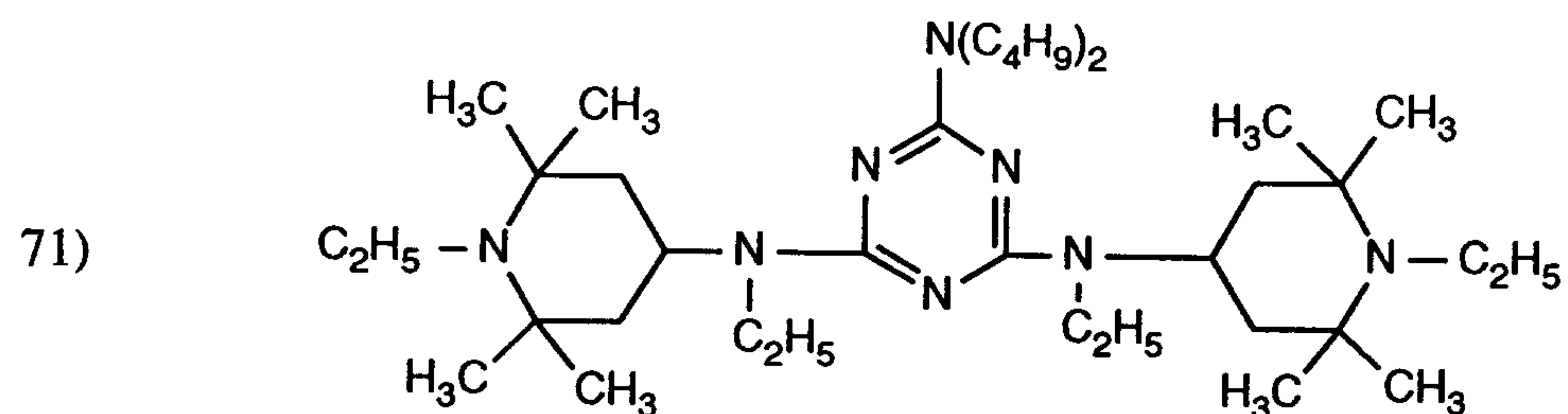
C_2 - C_6 alkylene A is, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene or hexamethylene.

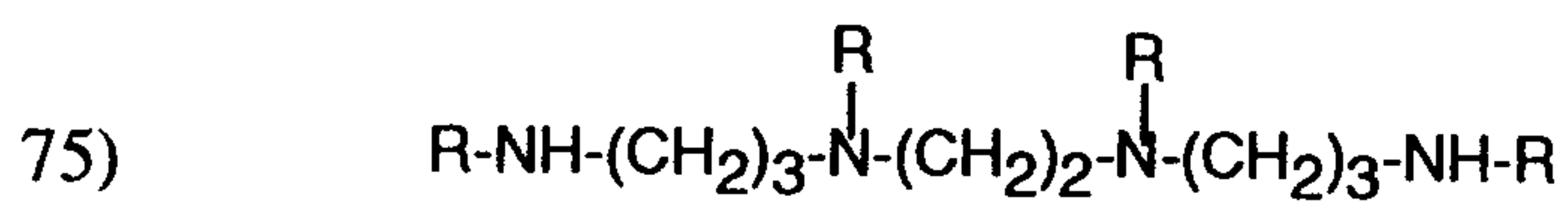
If G^{21} and G^{22} together are C_4 - C_5 alkylene or oxaalkylene, they are, for example, tetramethylene, pentamethylene or 3-oxapentamethylene.

Examples of polyalkylpiperidine compounds from this class are the compounds of the following formulae:

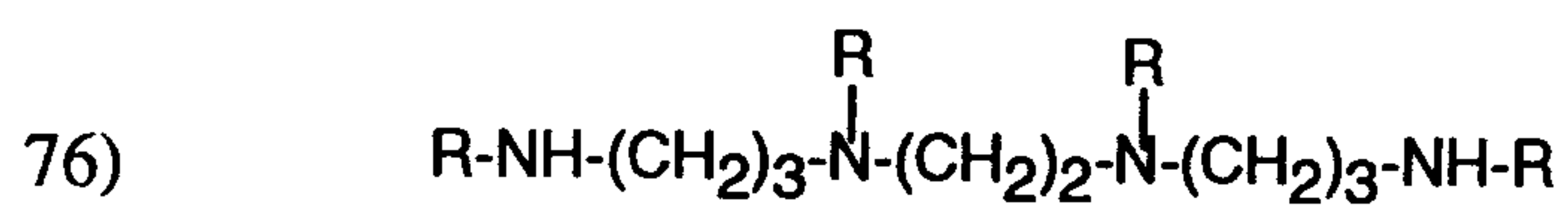
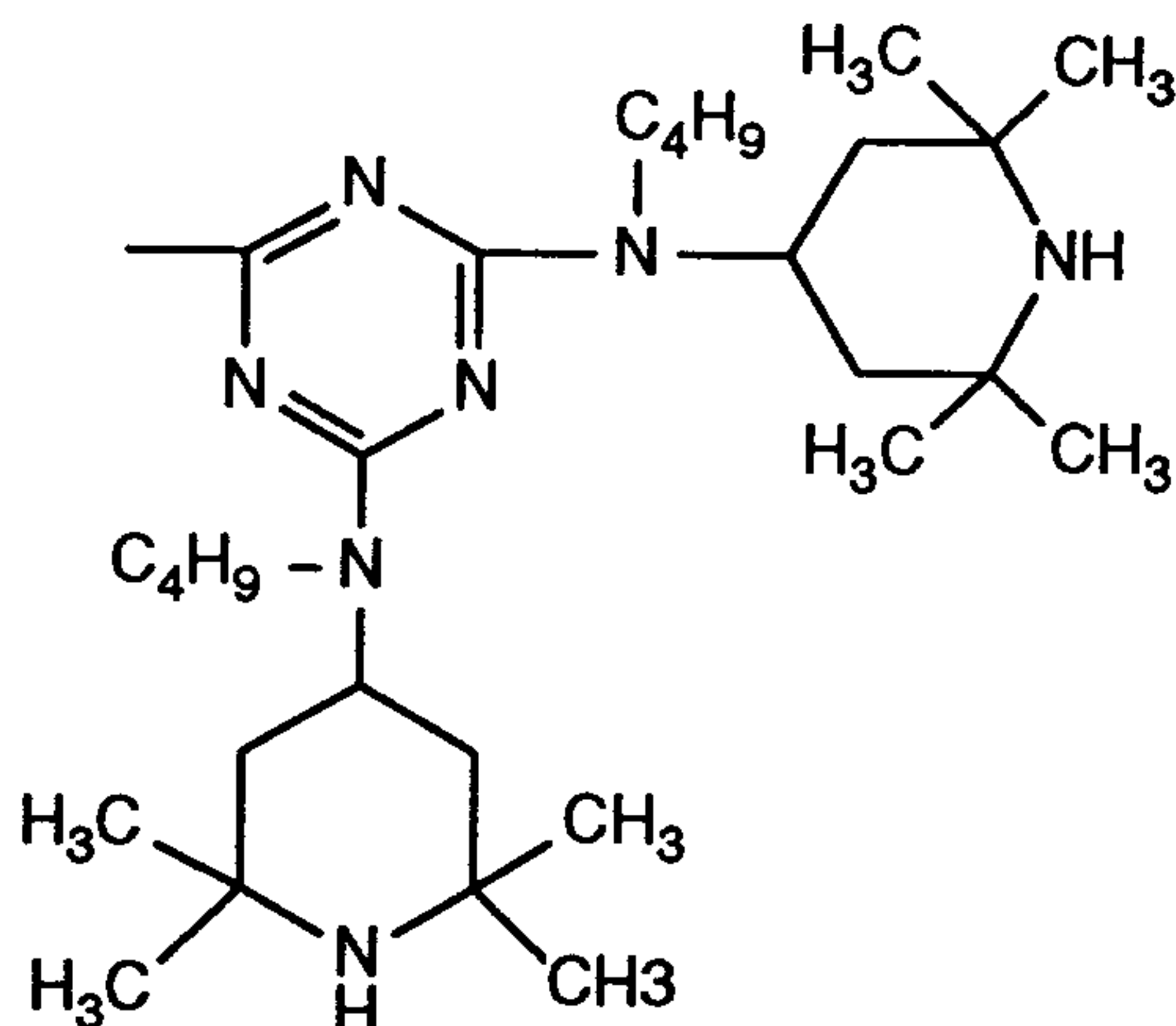
70)





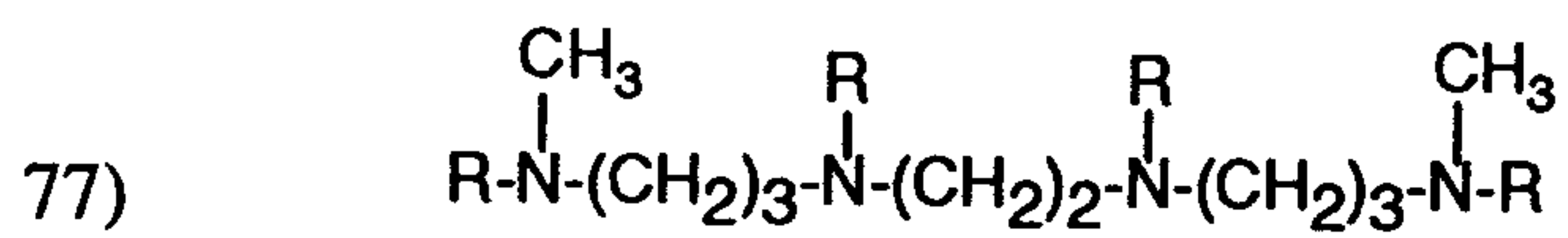
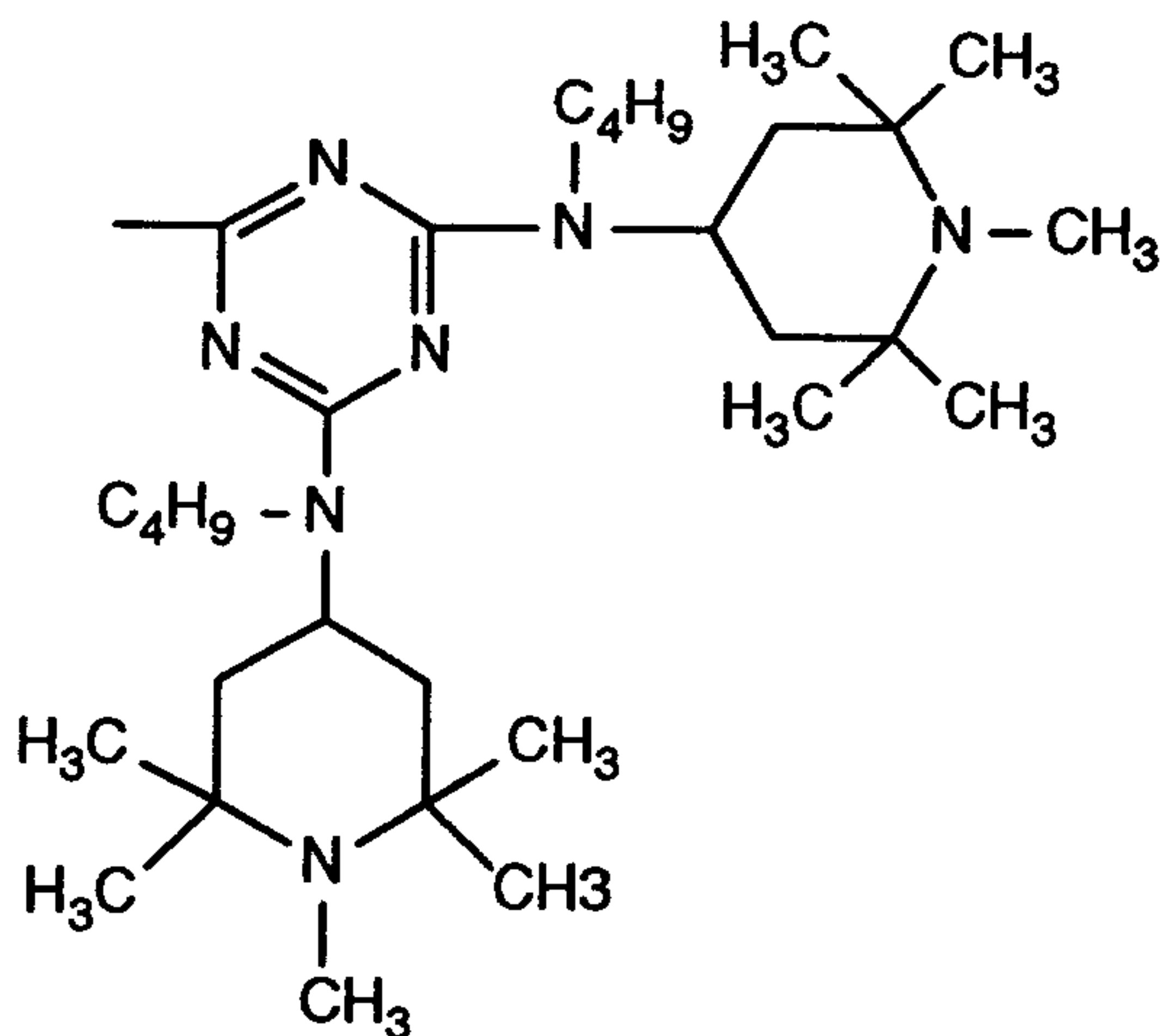


where R =

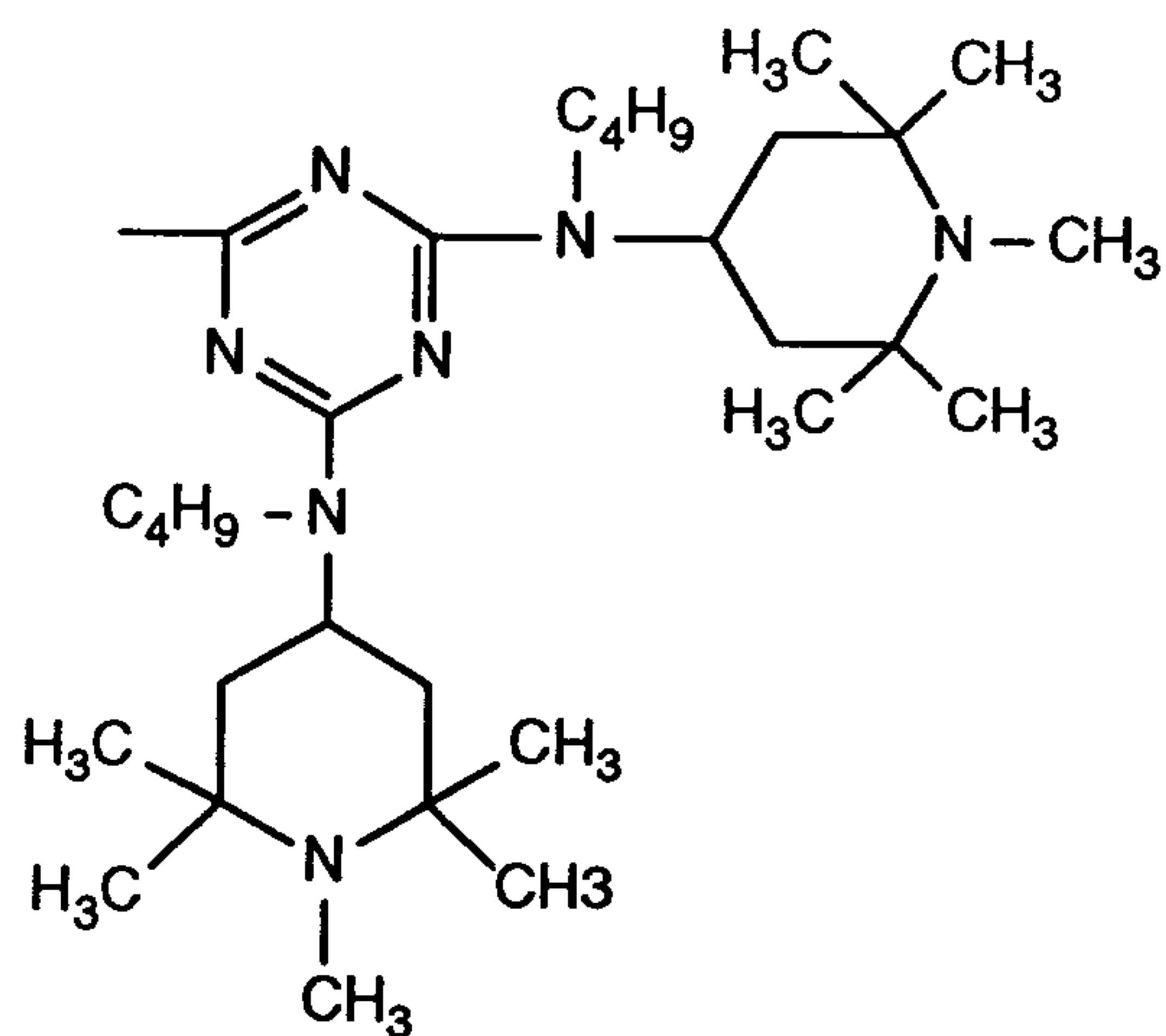


(amine J)

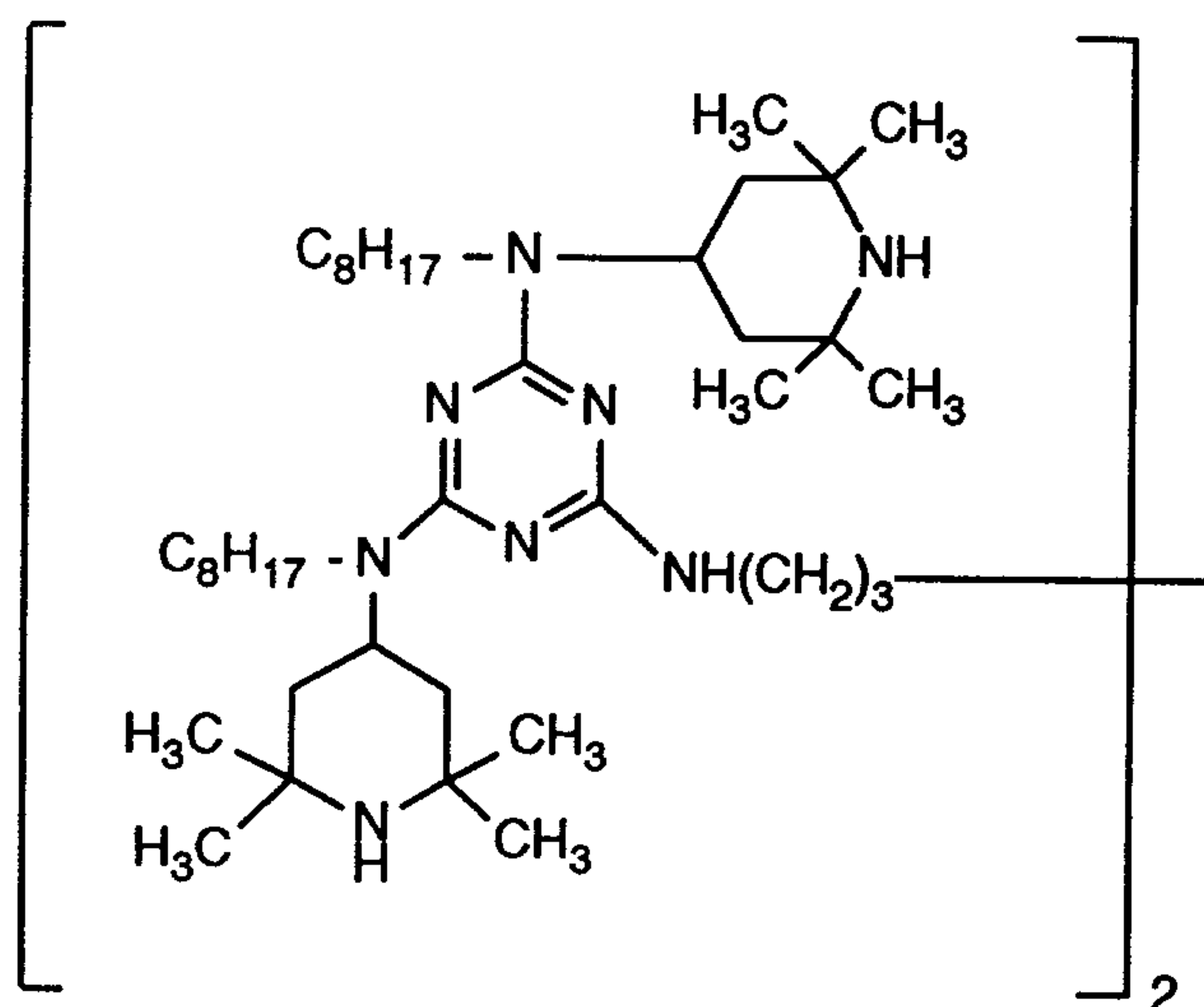
where R =



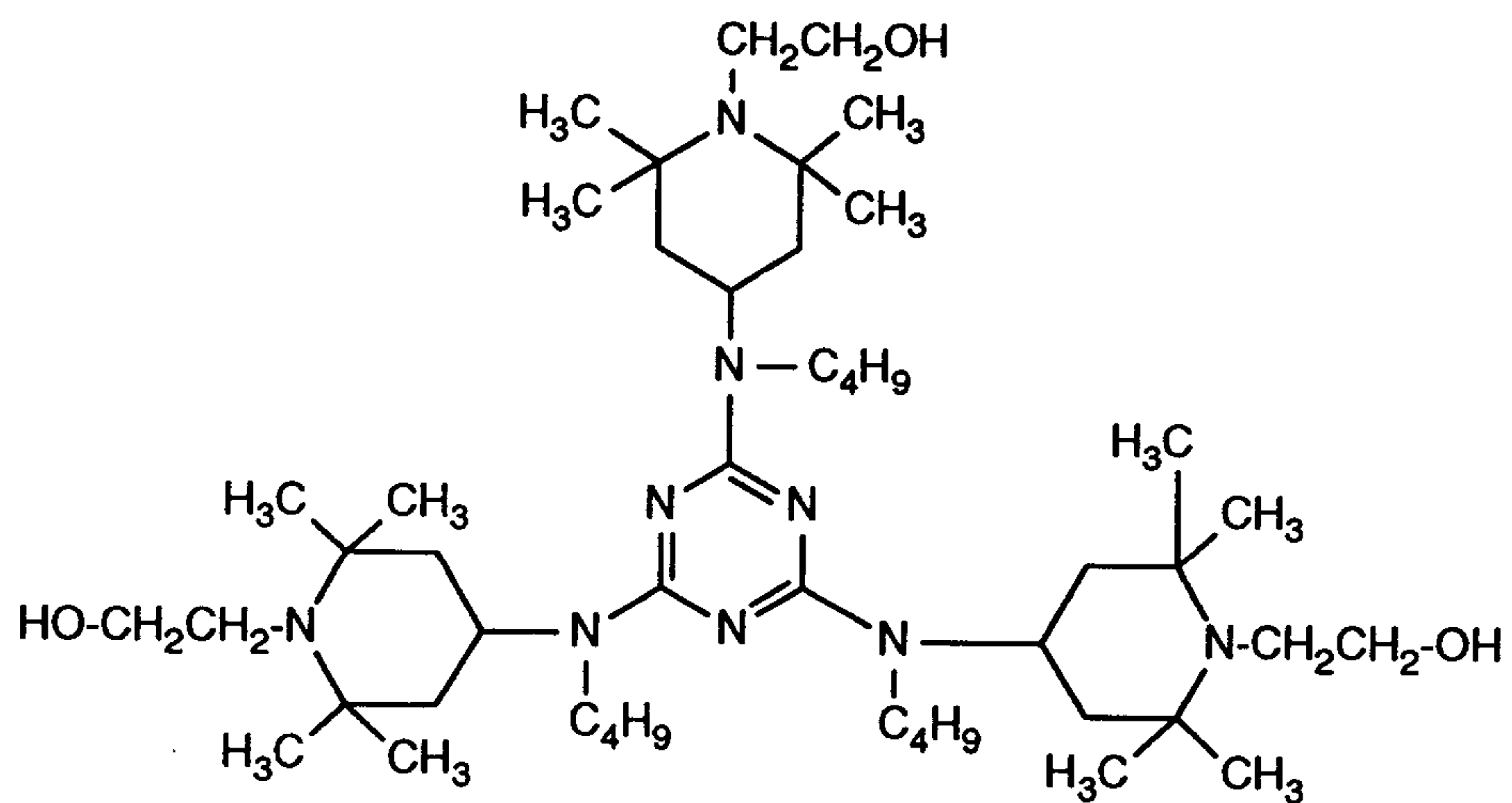
where R =



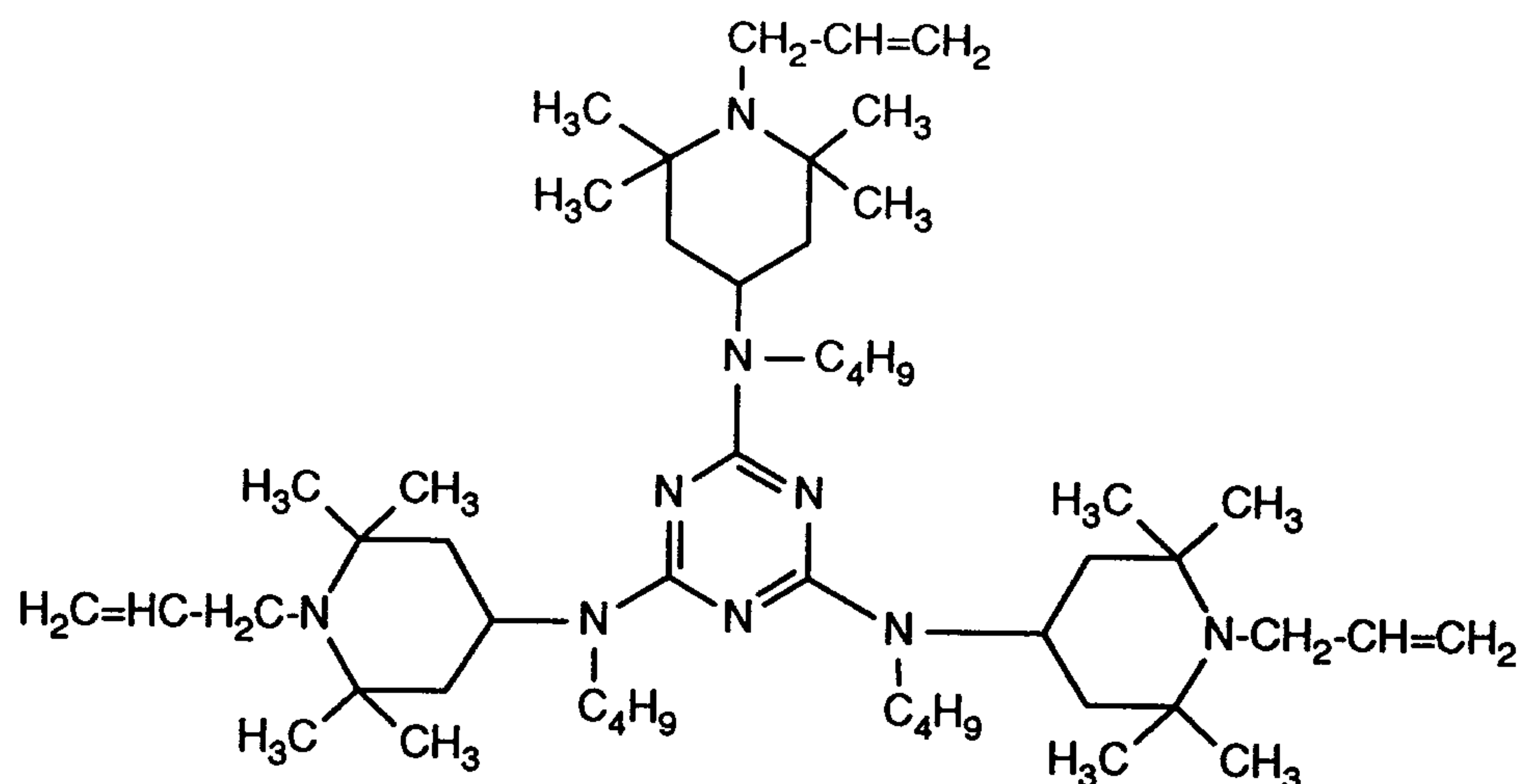
78)



79)

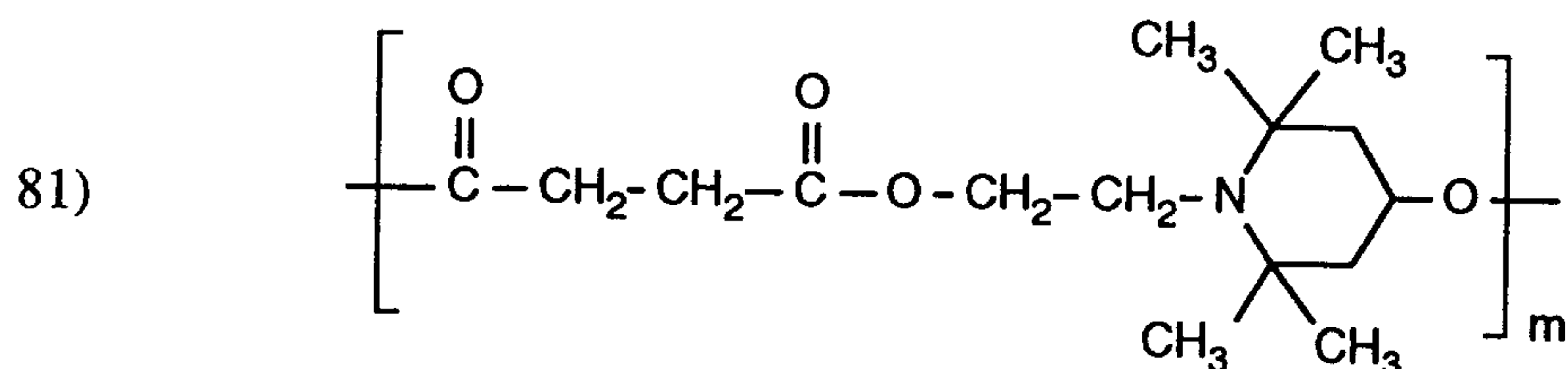


80)

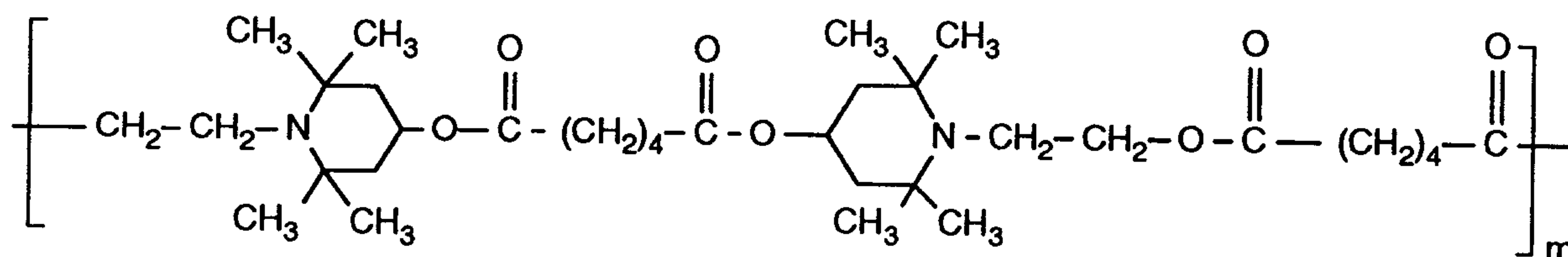


(f') Oligomeric or polymeric compounds whose recurring structural unit contains a 2,2,6,6-tetraalkylpiperidiny radical, in particular polyesters, polyethers, polyamides, polyamines, polyurethanes, polyureas, polyaminotriazines, poly(meth)acrylates, poly(meth)acrylamides and copolymers thereof which contain such radicals.

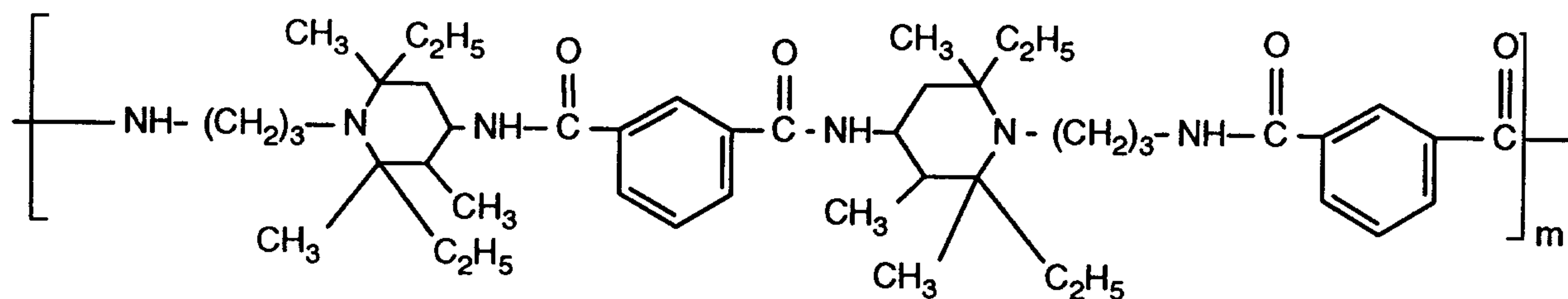
Examples of 2,2,6,6-polyalkylpiperidine compounds from this class are the compounds of the following formulae, where m is a number from 2 to about 200:



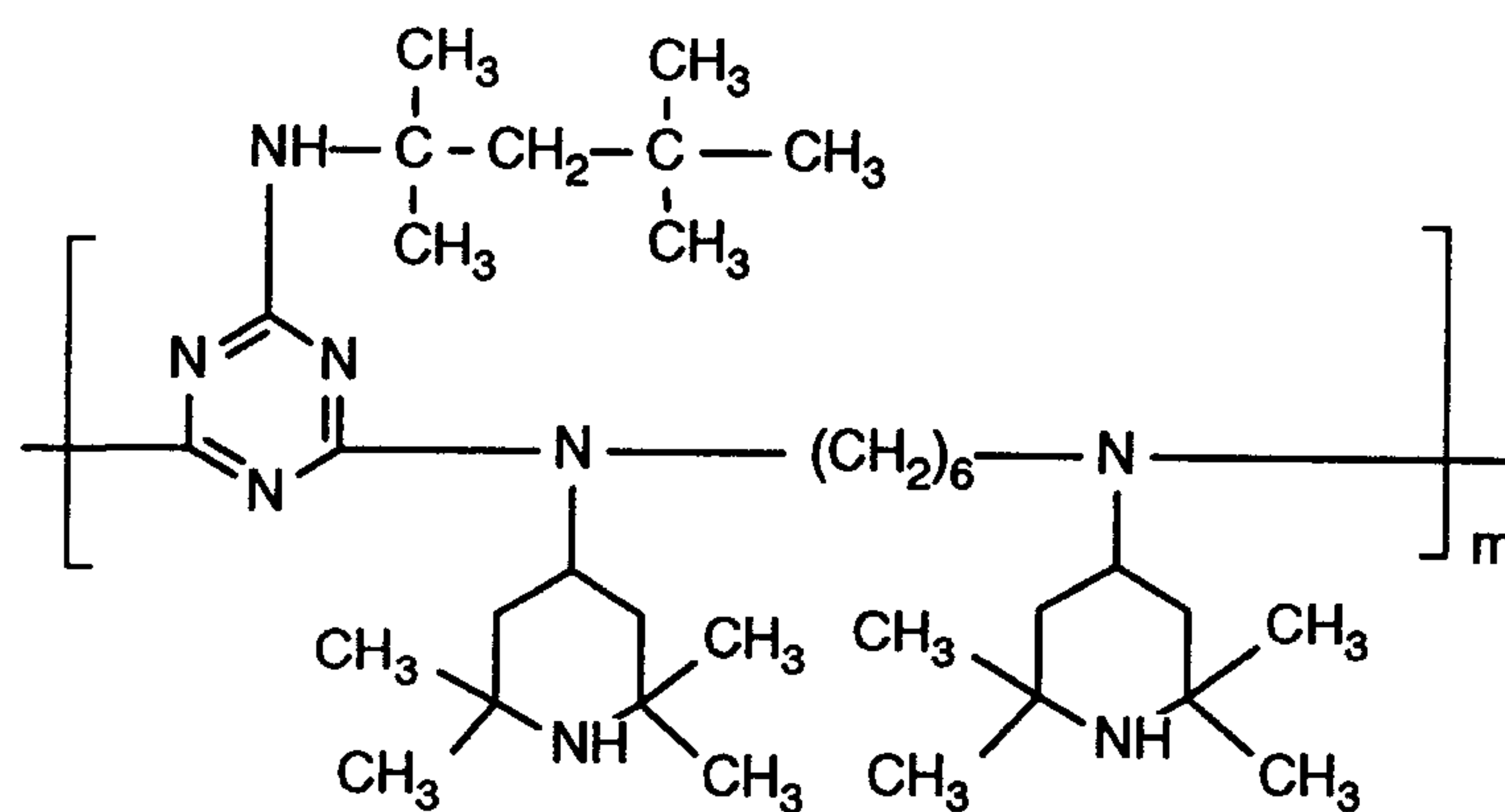
82)



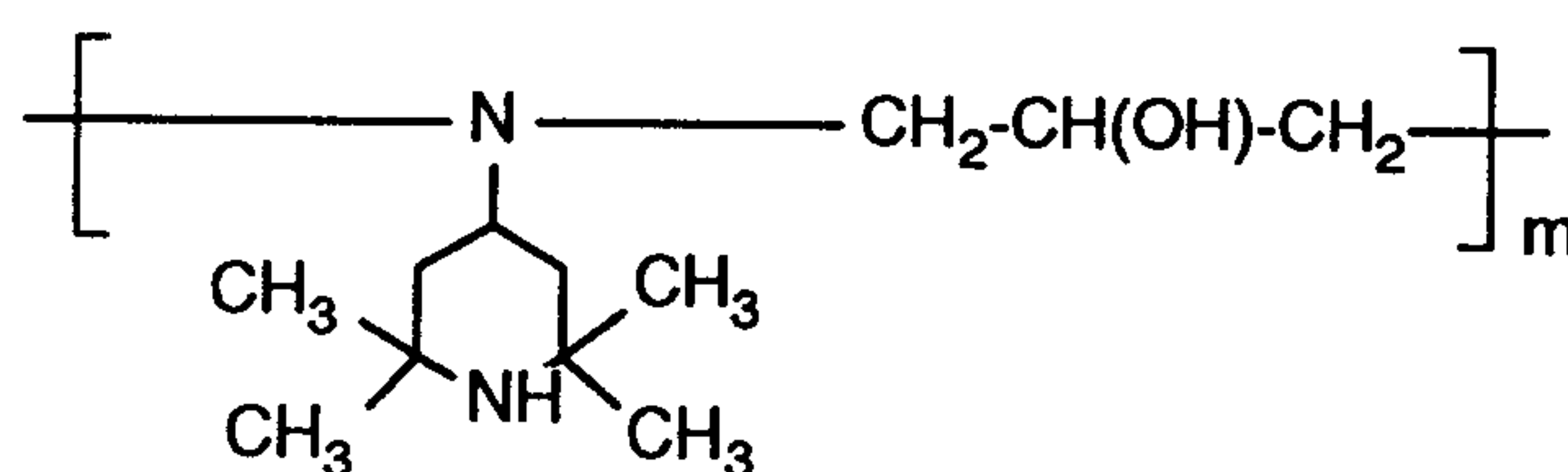
83)



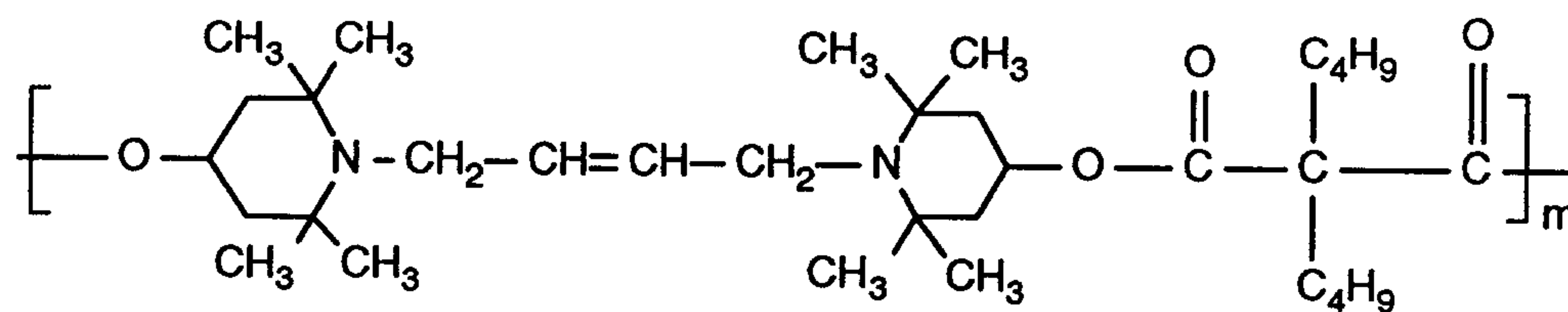
84)



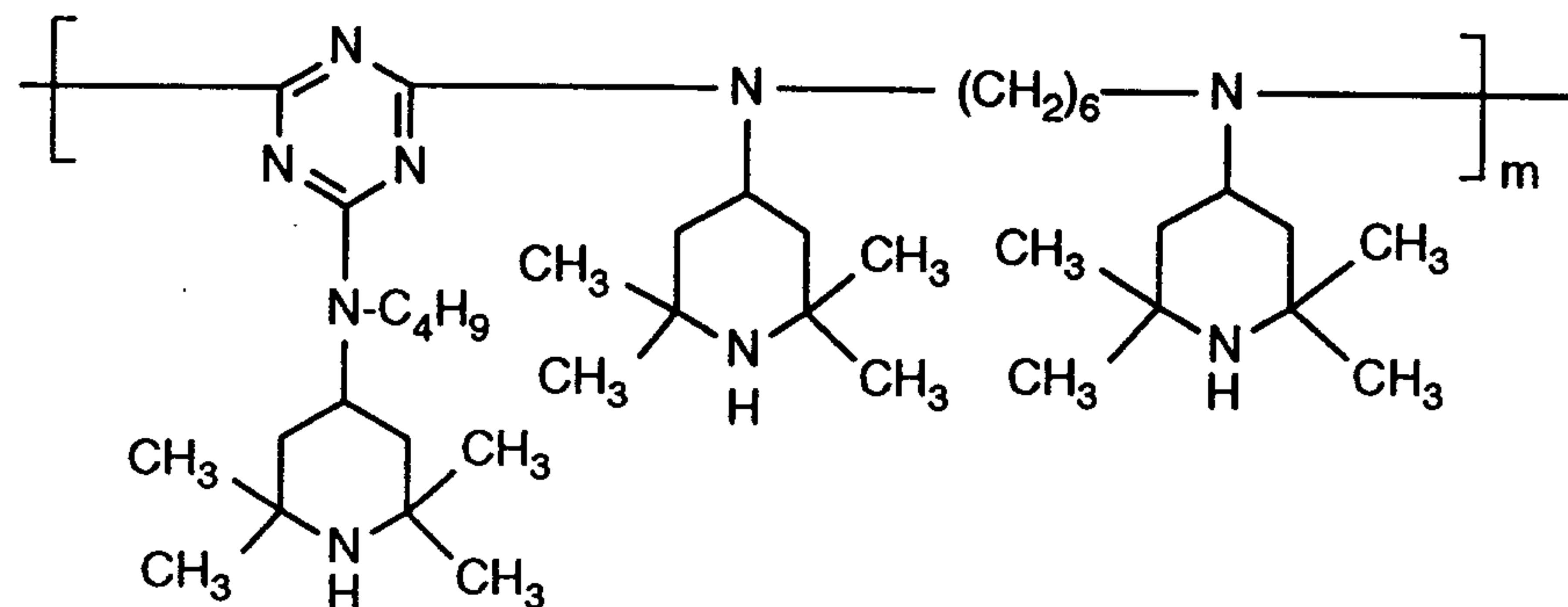
85)

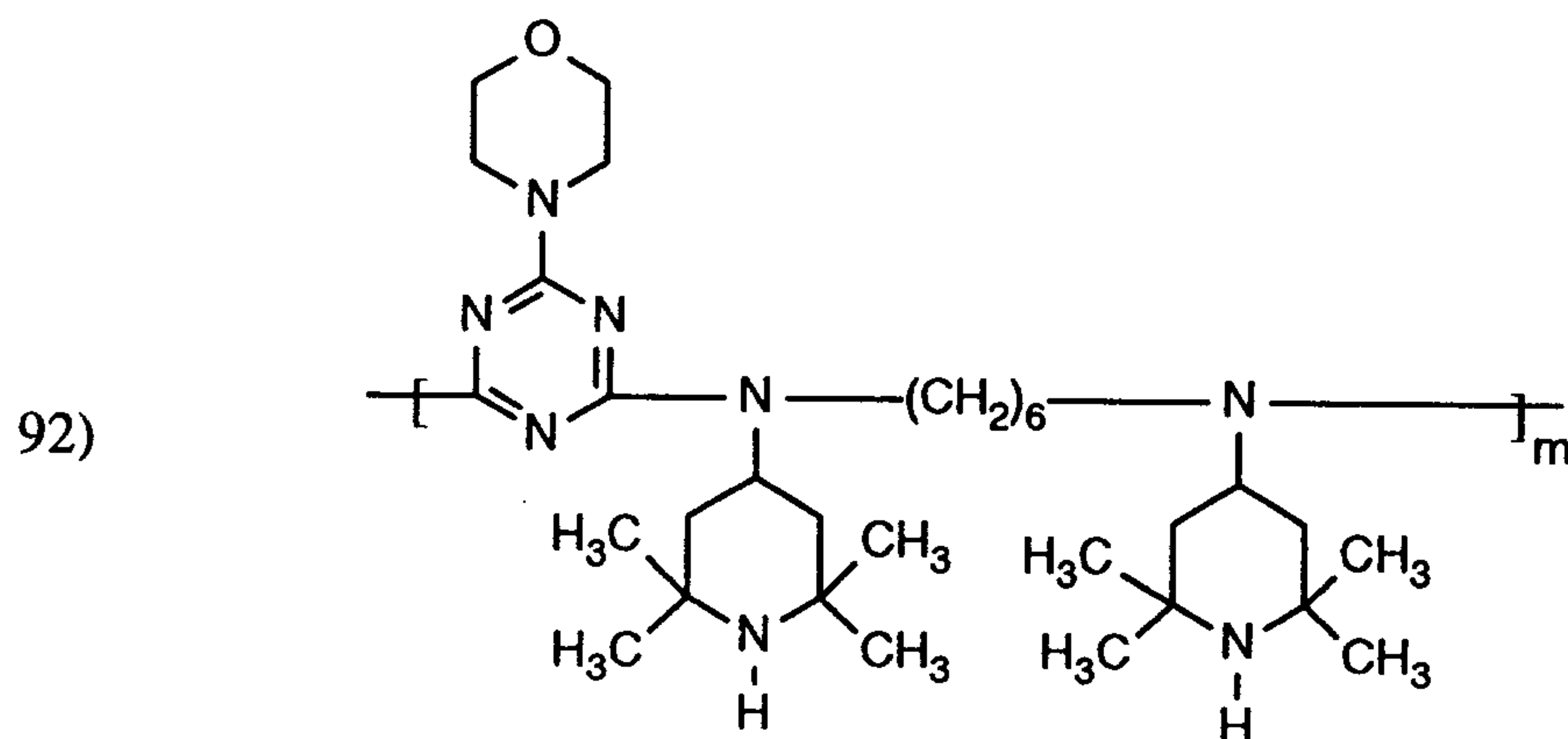
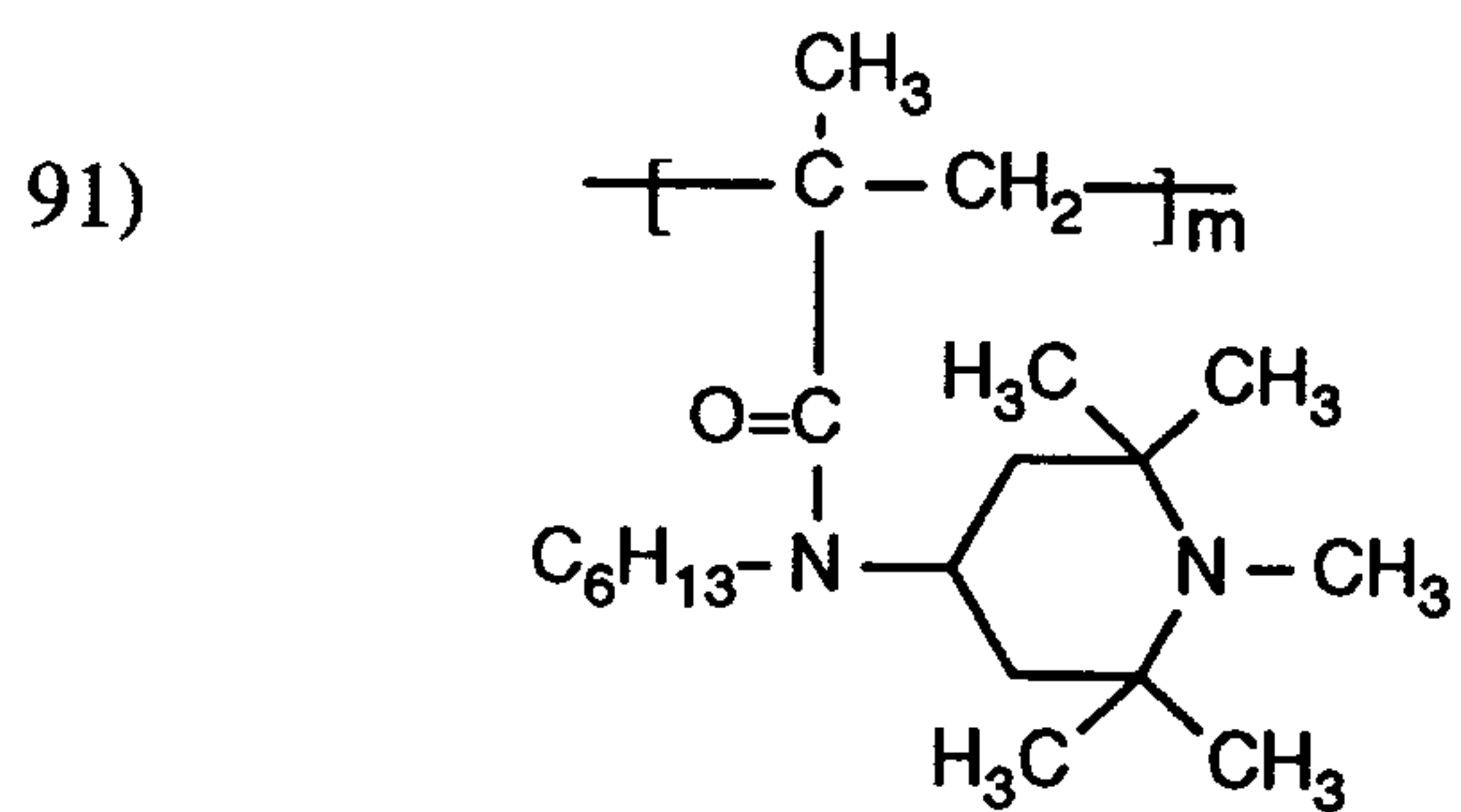
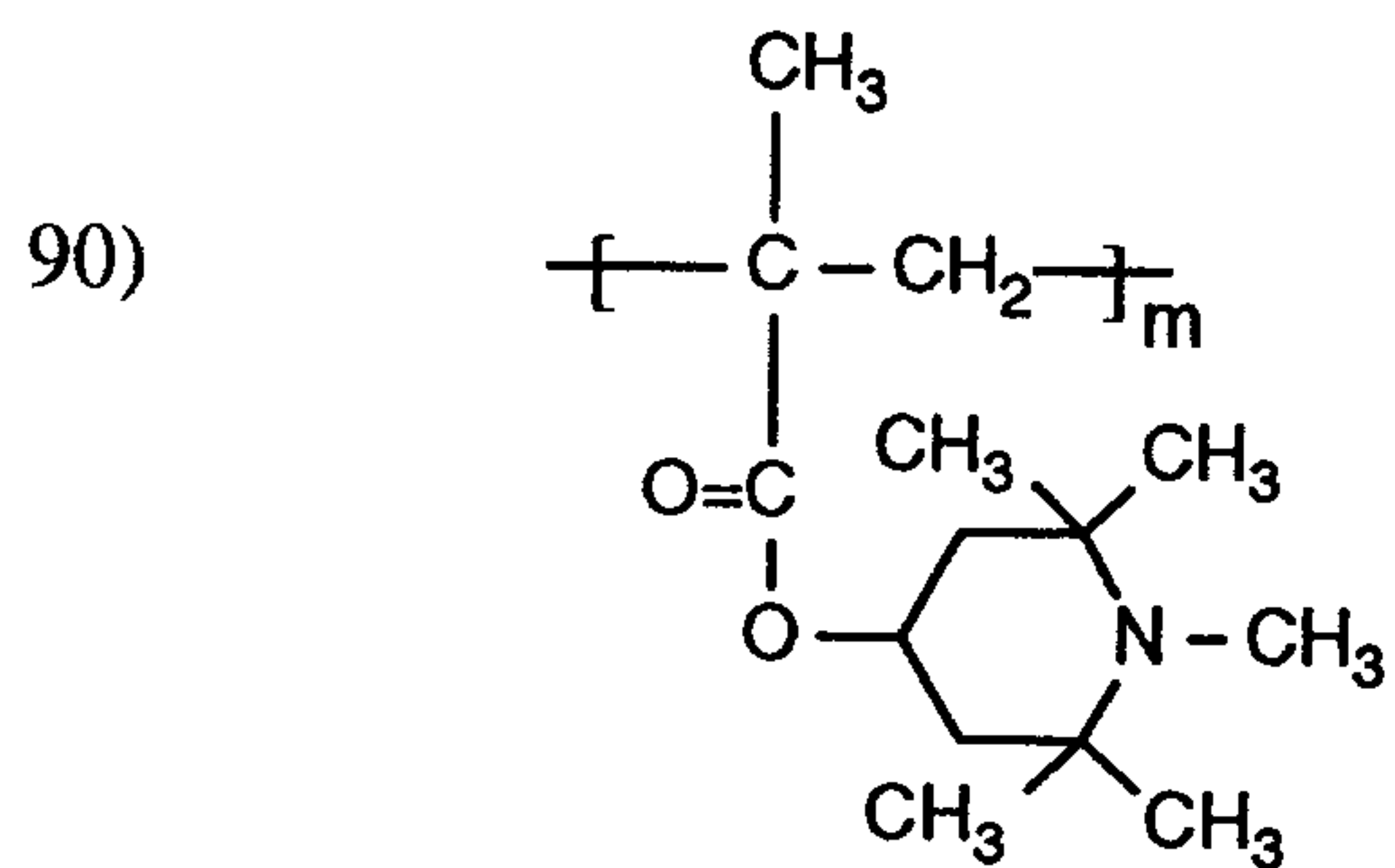
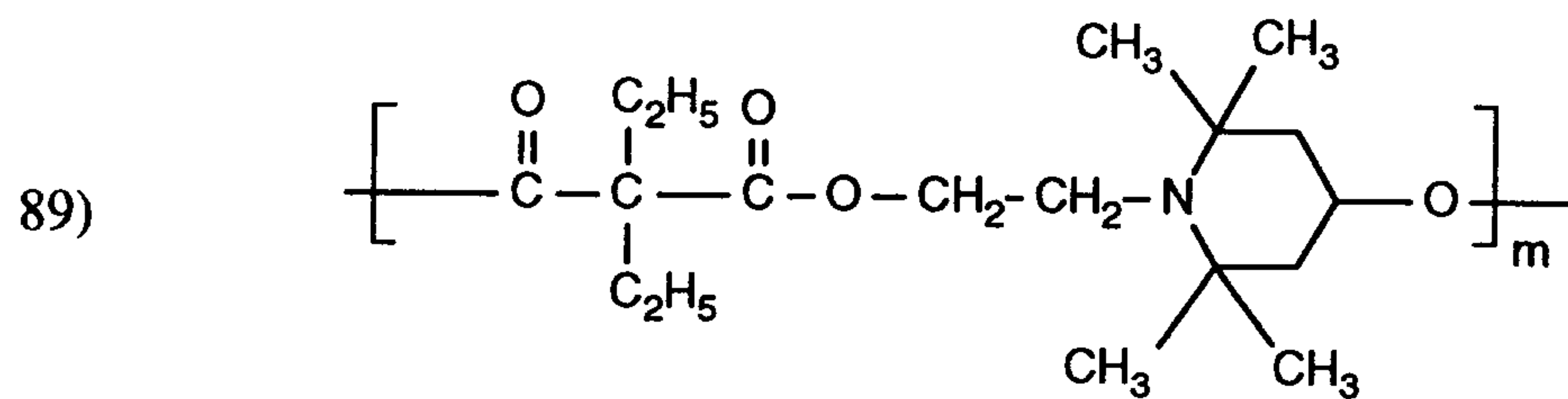
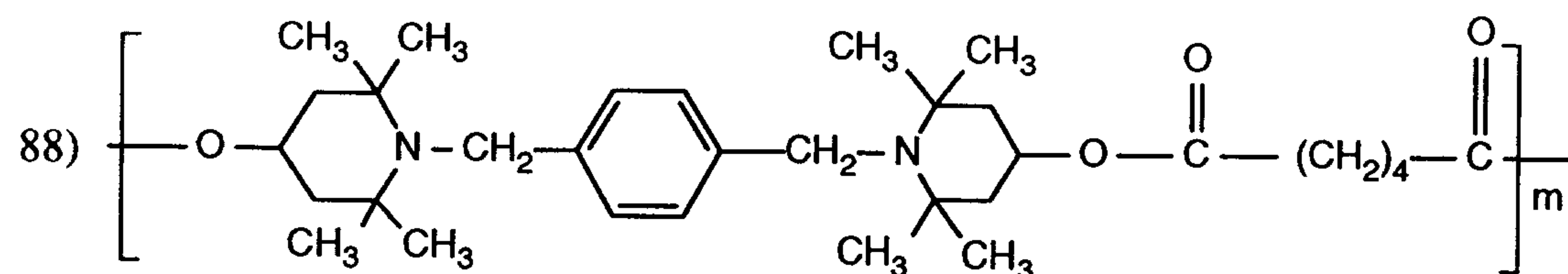


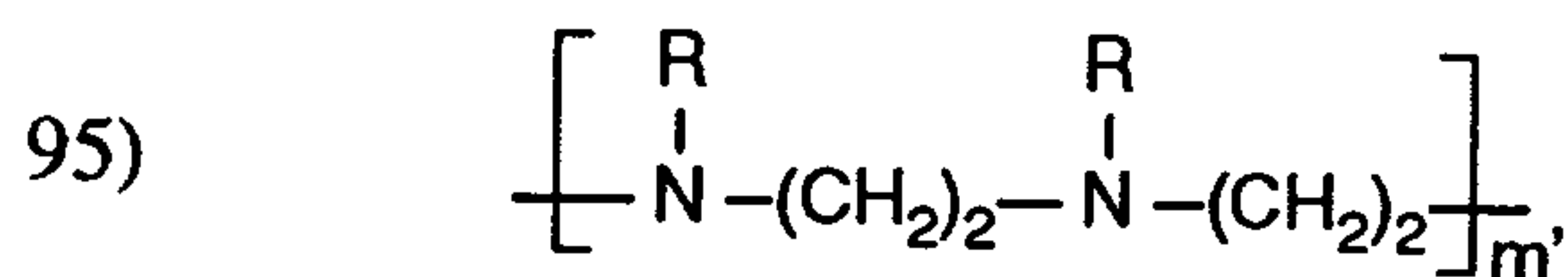
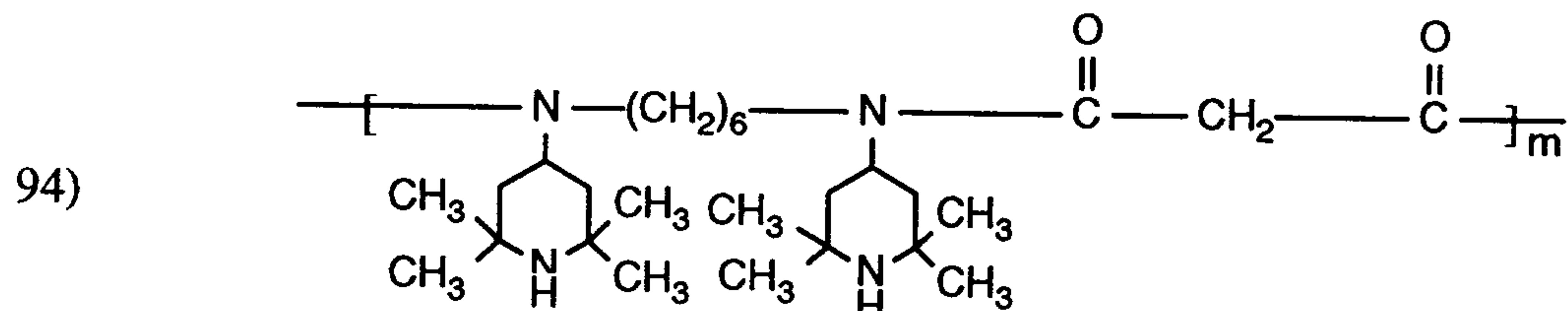
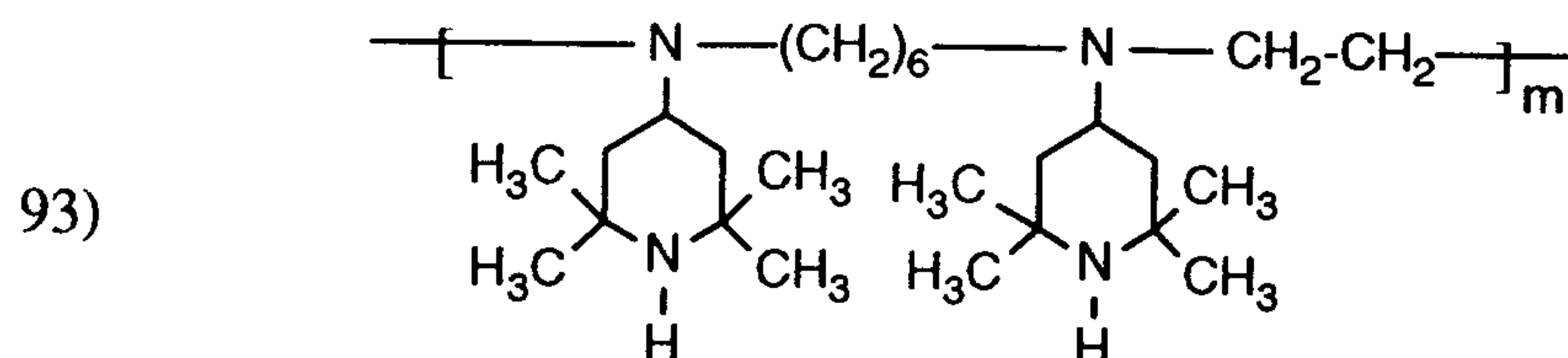
86)



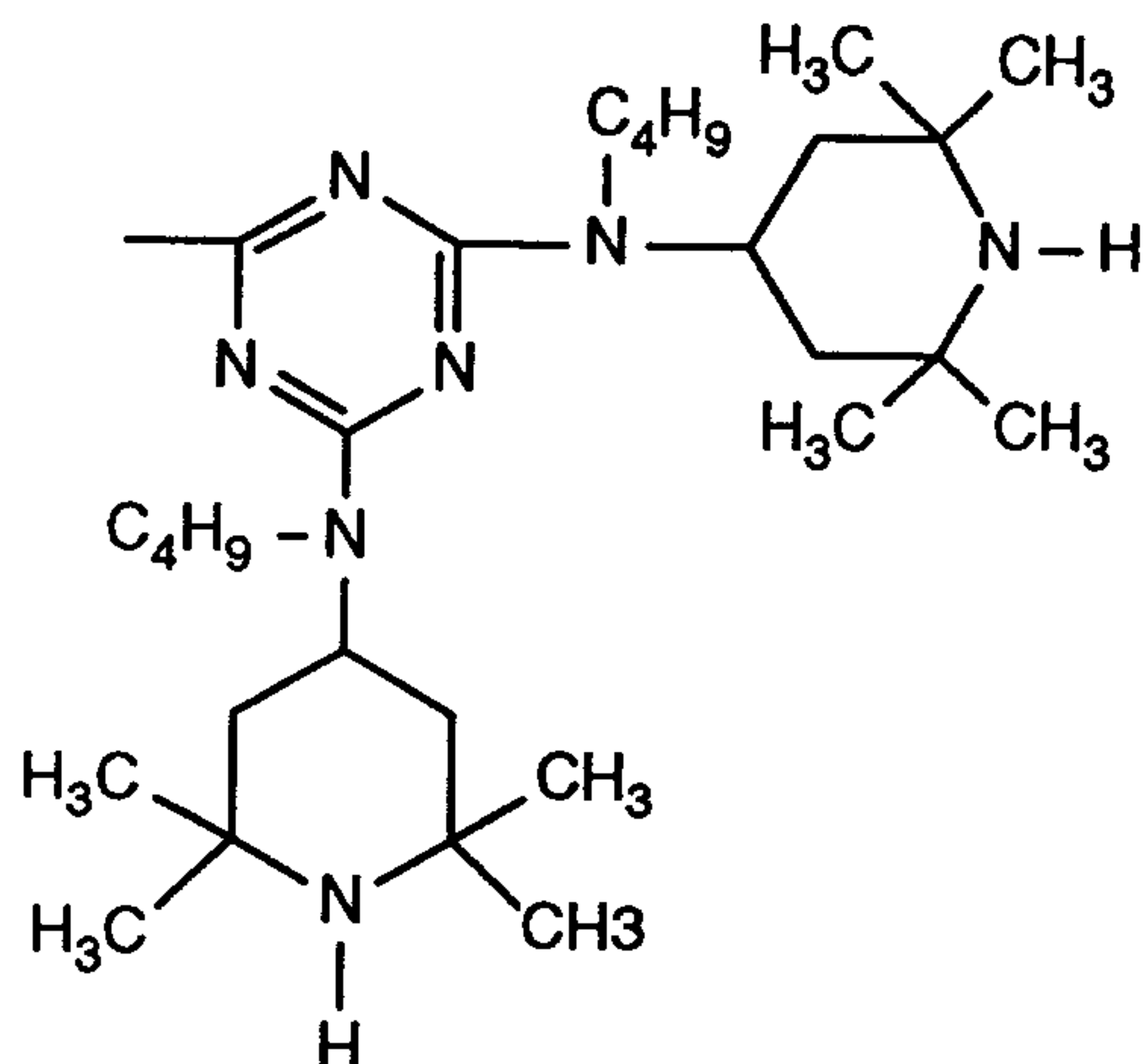
87)





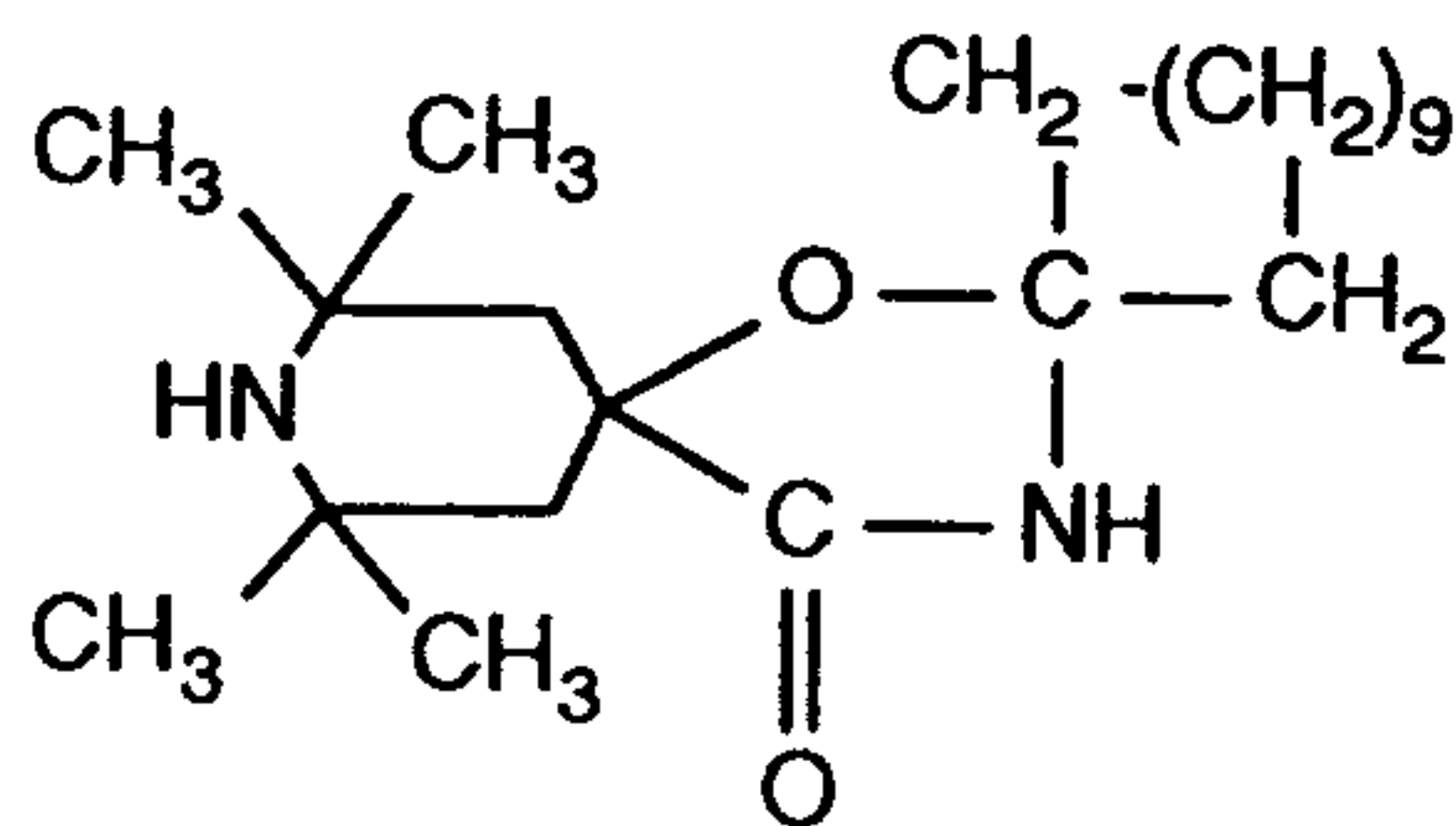


where R =

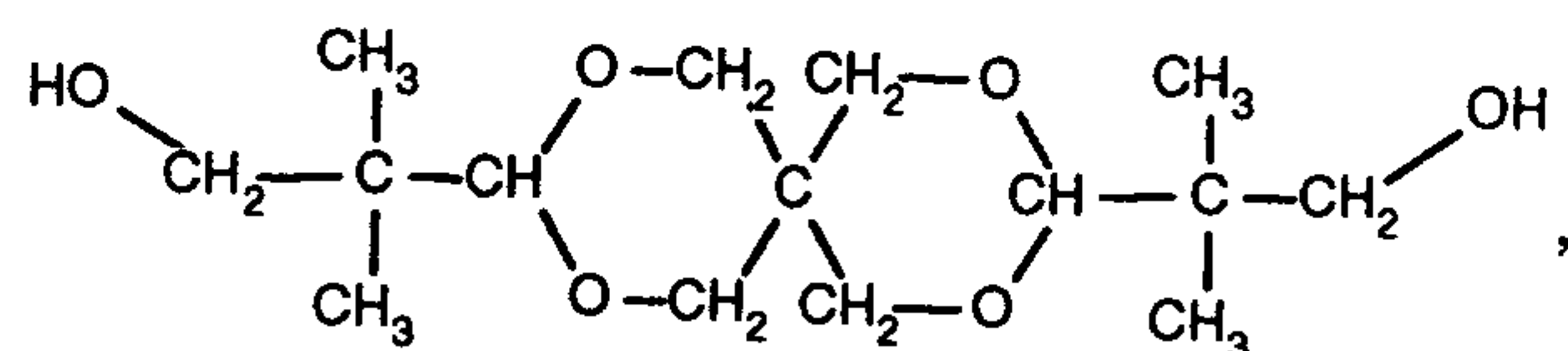


branch in the $\left[\text{N}(\text{CH}_2)_2 \right]_{m'}$ chain, m' and m'' are each an integer in the range from 0-200, with the proviso that $m' + m'' = m$.

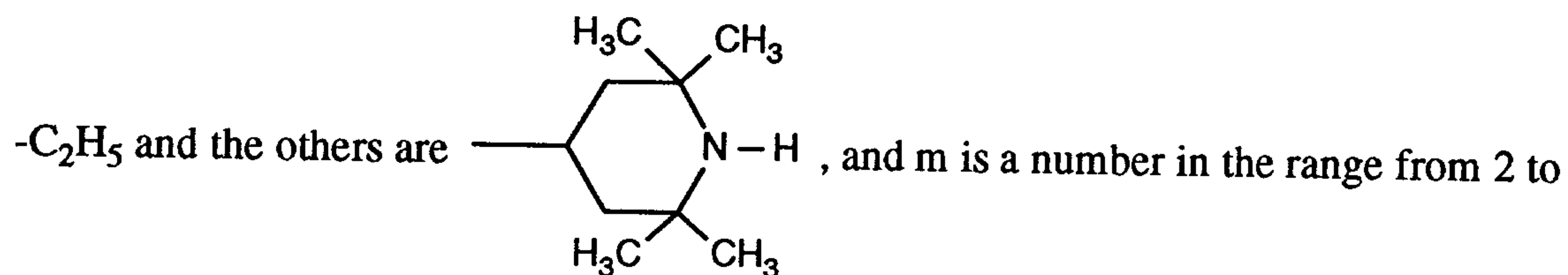
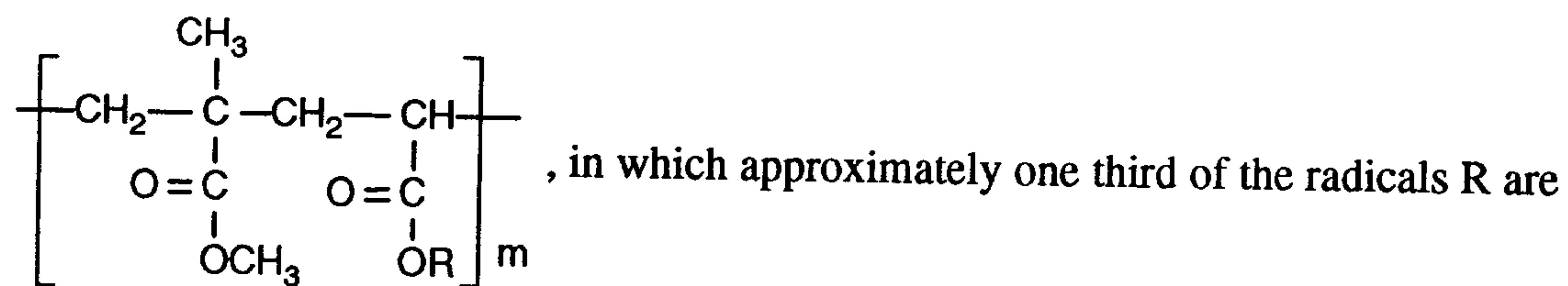
Further examples of polymeric compounds are products of the reaction of compounds of the formula

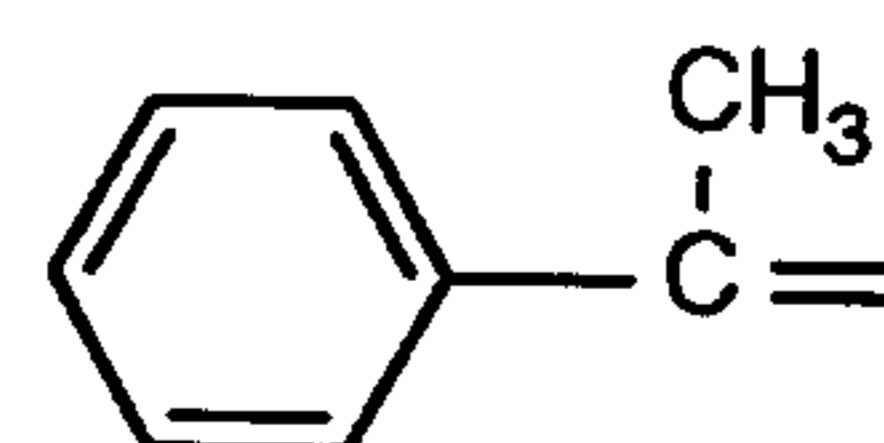


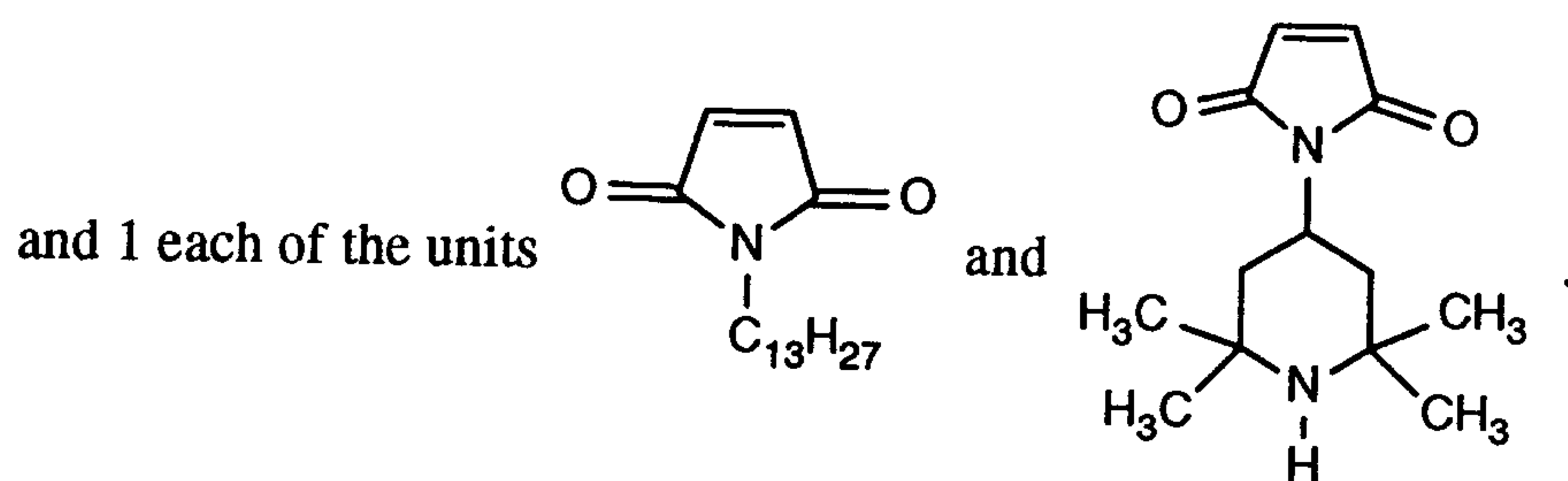
with epichlorohydrin; polyesters made from butane-1,2,3,4-tetracarboxylic acid with a bifunctional alcohol of the formula



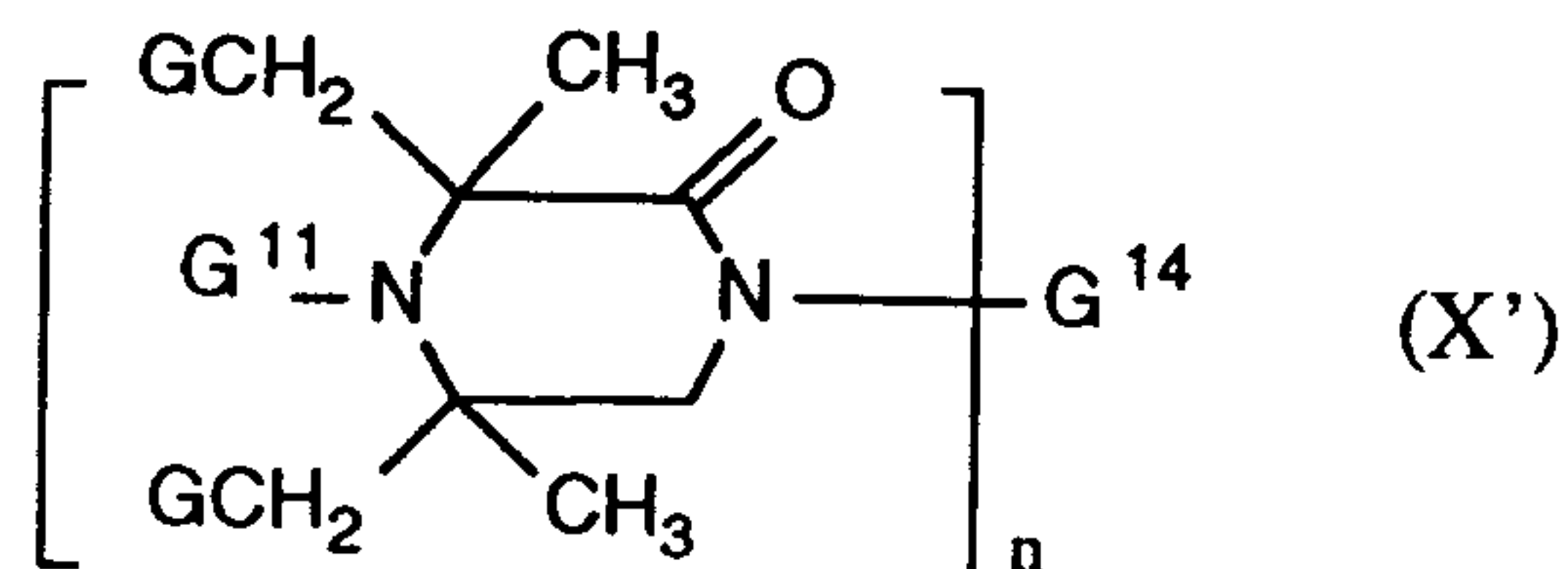
whose carboxyl side chains originating from the tetracarboxylic acid has been esterified by means of 2,2,6,6-tetramethyl-4-hydroxypiperidine; compounds of the formula



200; or copolymers whose recurring unit is built up from 2  units



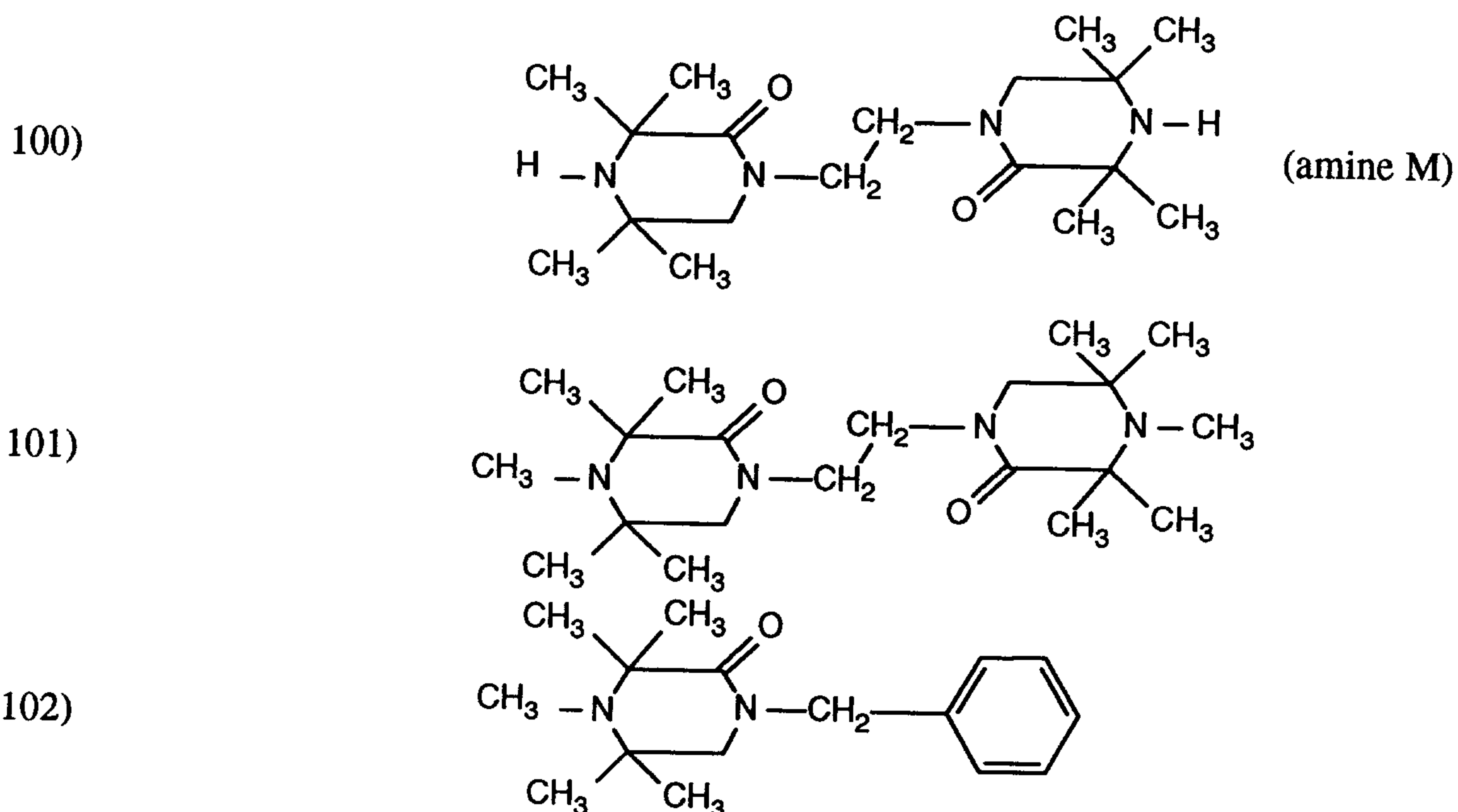
(g') Compounds of the formula X'



in which n is the number 1 or 2, G and G¹¹ are as defined under (a'), and G¹⁴ is as defined

under (b'), but G^{14} cannot be $-\text{CONH-Z}$ and $-\text{CH}_2\text{-CH(OH)-CH}_2\text{-O-D-O-}$.

Examples of such compounds are the following:



Of interest are compositions comprising as component (c)(ii) or component (c)(iii)(y) a compound of the formula IV' in which n is an integer in the range from 1 to 4, G and G^1 are hydrogen, and

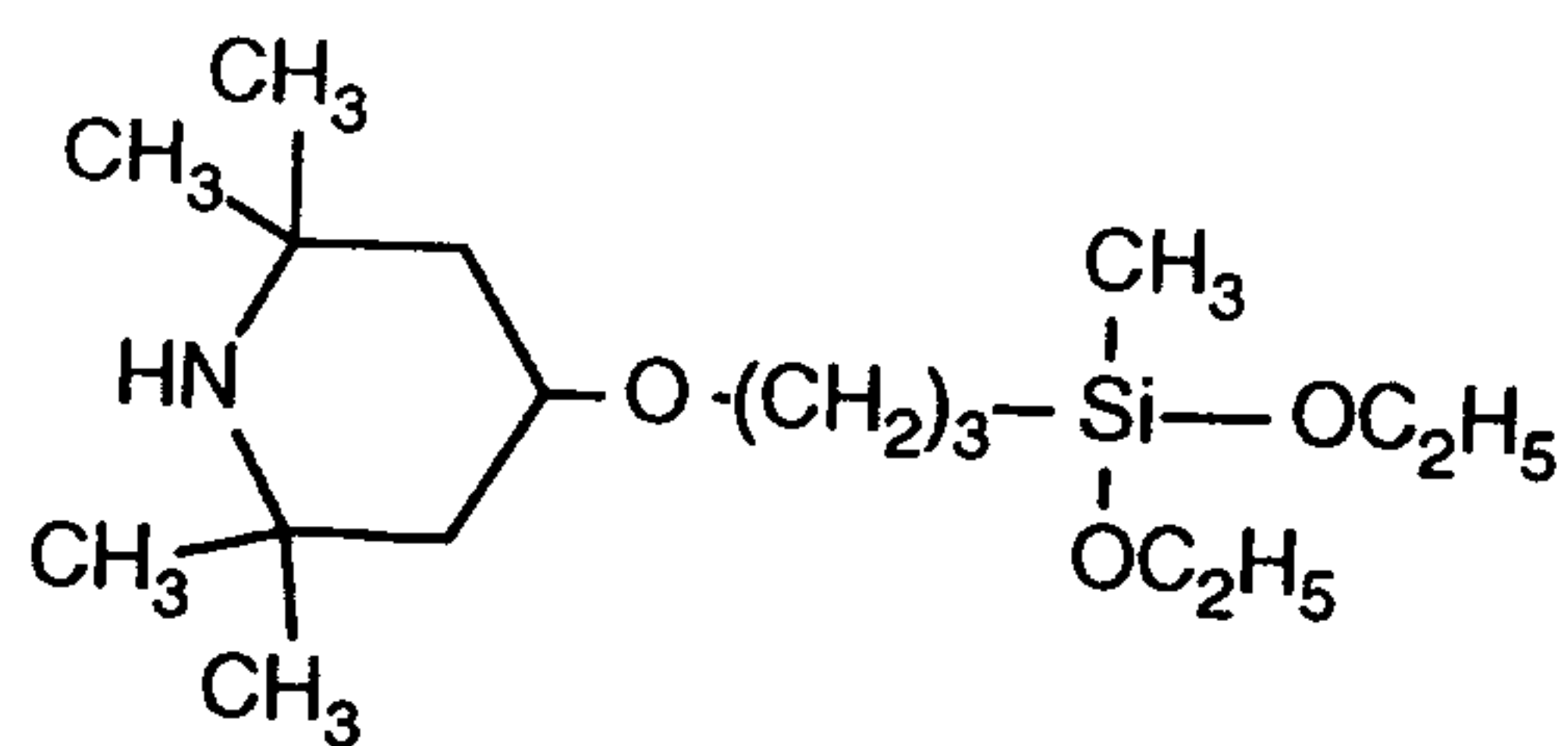
G^{11} is hydrogen or $\text{C}_1\text{-C}_{18}$ alkyl, and

G^{12} , if $n = 1$, is a radical of the formula $-(\text{C}_j\text{H}_{2j})\text{-Si(Z')}_2\text{Z}''$, in which j is an integer in the range from 2 to 5, and Z' and Z'' , independently of one another, are $\text{C}_1\text{-C}_4$ alkyl or $\text{C}_1\text{-C}_4$ alkoxy, and

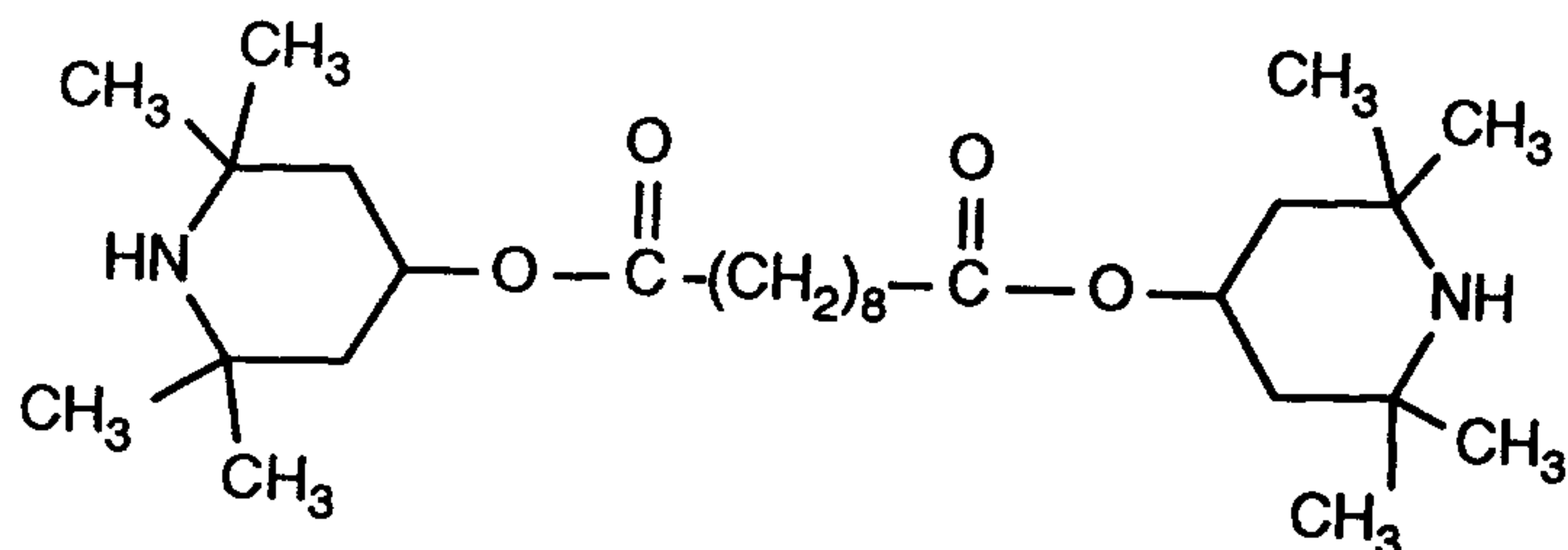
G^{12} , if $n = 2$, is a radical of an aliphatic dicarboxylic acid having 2 to 12 carbon atoms, which may be substituted by $-\text{COOZ}^{12}$, where Z^{12} is $\text{C}_1\text{-C}_{20}$ alkyl,

G^{12} , if $n = 3$, is a radical of an aromatic tricarboxylic acid having 9 to 15 carbon atoms,

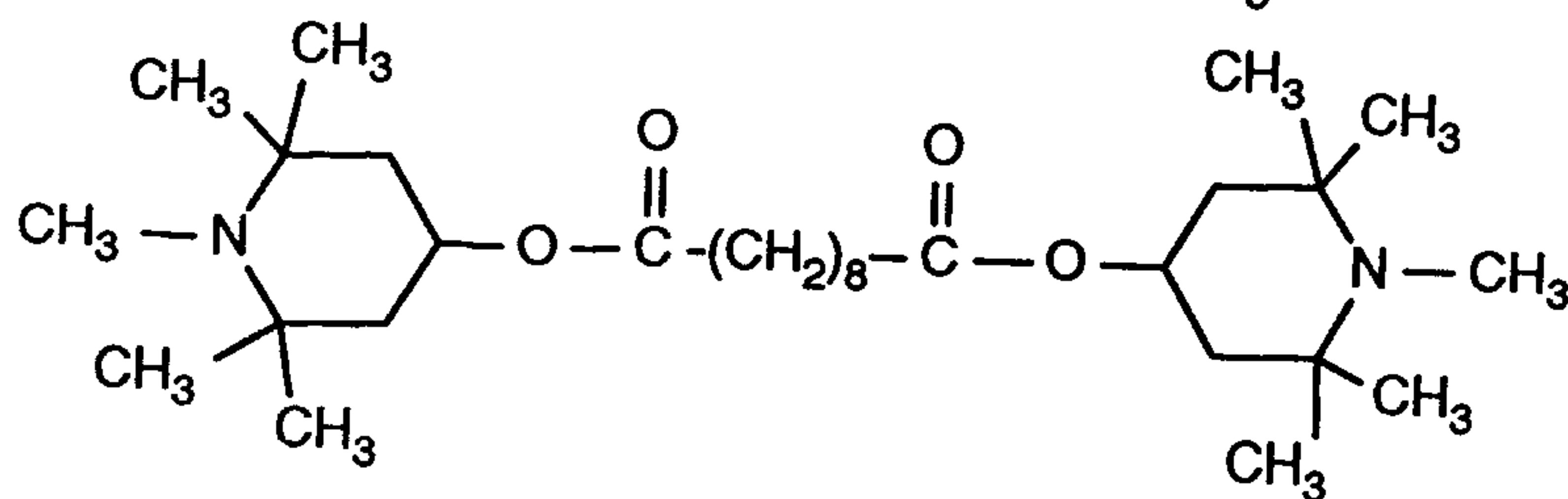
G^{12} , if $n = 4$, is a radical of an aliphatic tetracarboxylic acid having 8 to 12 carbon atoms; amines of particular industrial interest from this class are those of the formulae



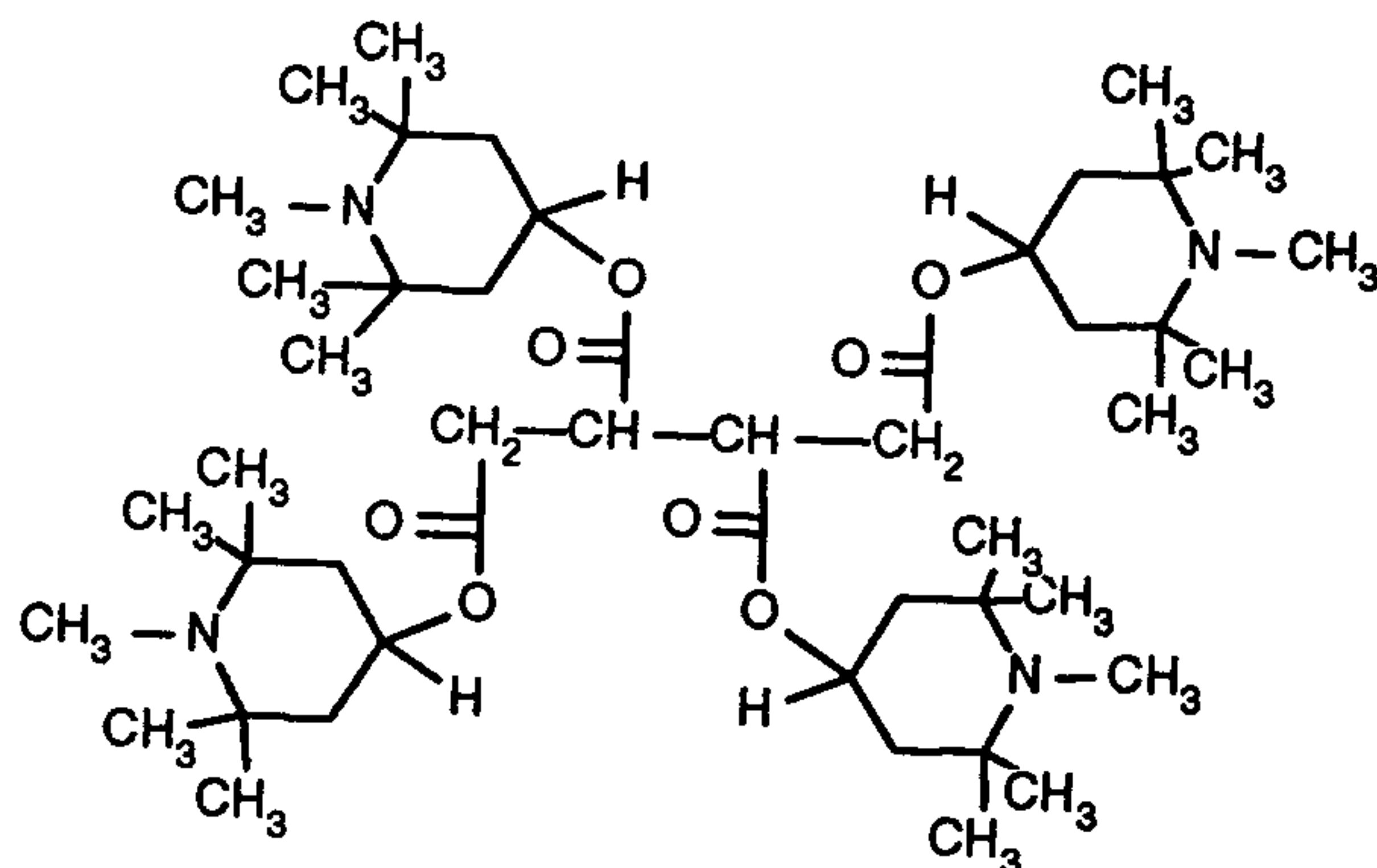
(amine B),



(amine C),



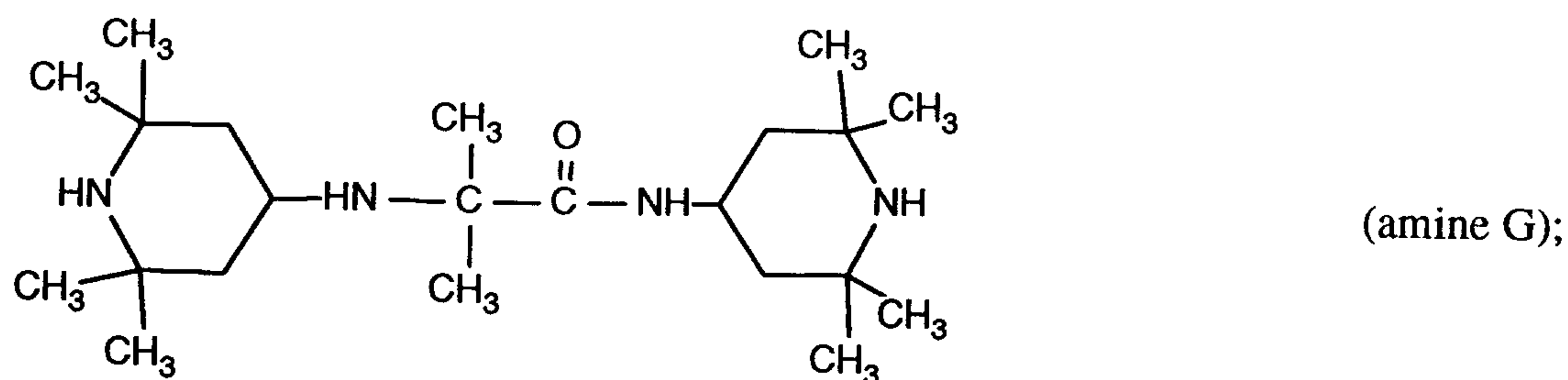
(amine D),



(amine E),

and esters of butane-1,2,3,4-tetracarboxylic acid containing 2 1,2,2,6,6-pentamethyl-4-hydroxypiperidine units and 2 $C_{13}H_{27}-OH$ (amine F) units.

Likewise of interest are compositions comprising as component (c)(ii) or component (c)(iii)(y) a compound of the formula V' in which n is 2, G and G^1 are hydrogen, G^{11} is hydrogen or methyl, G^{13} is hydrogen or C_1-C_8 alkyl, and G^{14} is C_2-C_8 alkylene or 1-oxo- C_2-C_8 alkylene; an amine of particular industrial interest from this class is the compound of the formula

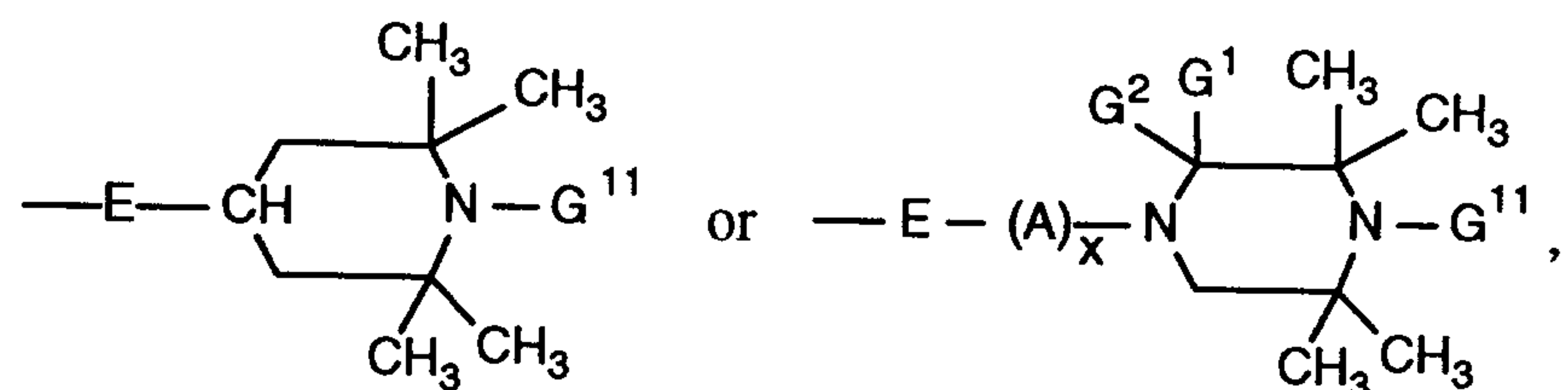


compounds of the formula VIIC in which n is 1, G , G^1 and G^{17} are hydrogen, G^{11} is hydrogen or methyl, and

T_1 and T_2 , together with the carbon atom bonding them, form a C_5 - C_{14} cycloalkane ring; an amine of particular industrial interest from this class is the compound of the formula



compounds of the formula VIII' in which n is 1 or 2, G^{18} and G^{19} are a group of the formula



G^{11} is hydrogen or methyl,

G^1 and G^2 are hydrogen or together are a substituent $=O$,

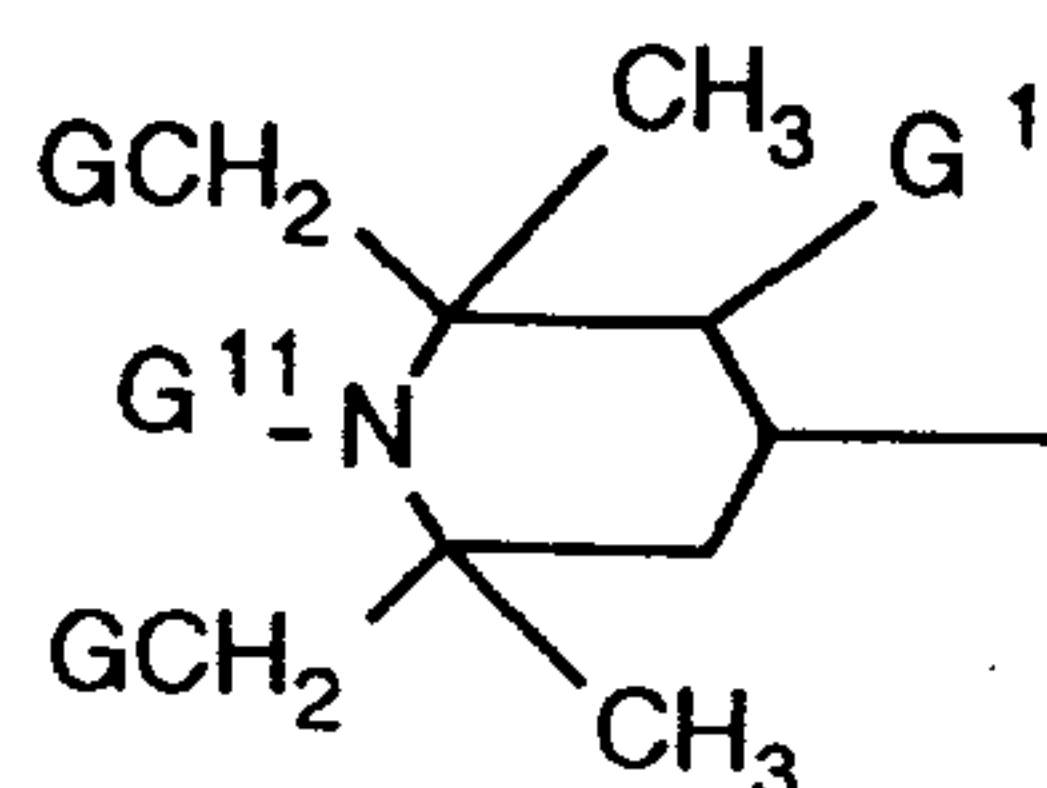
E is $-O-$ or $-NG^{13}-$, A is C_2 - C_6 alkylene and x is the number 0 or 1

G^{13} is hydrogen, C_1 - C_{12} alkyl or cyclohexyl,

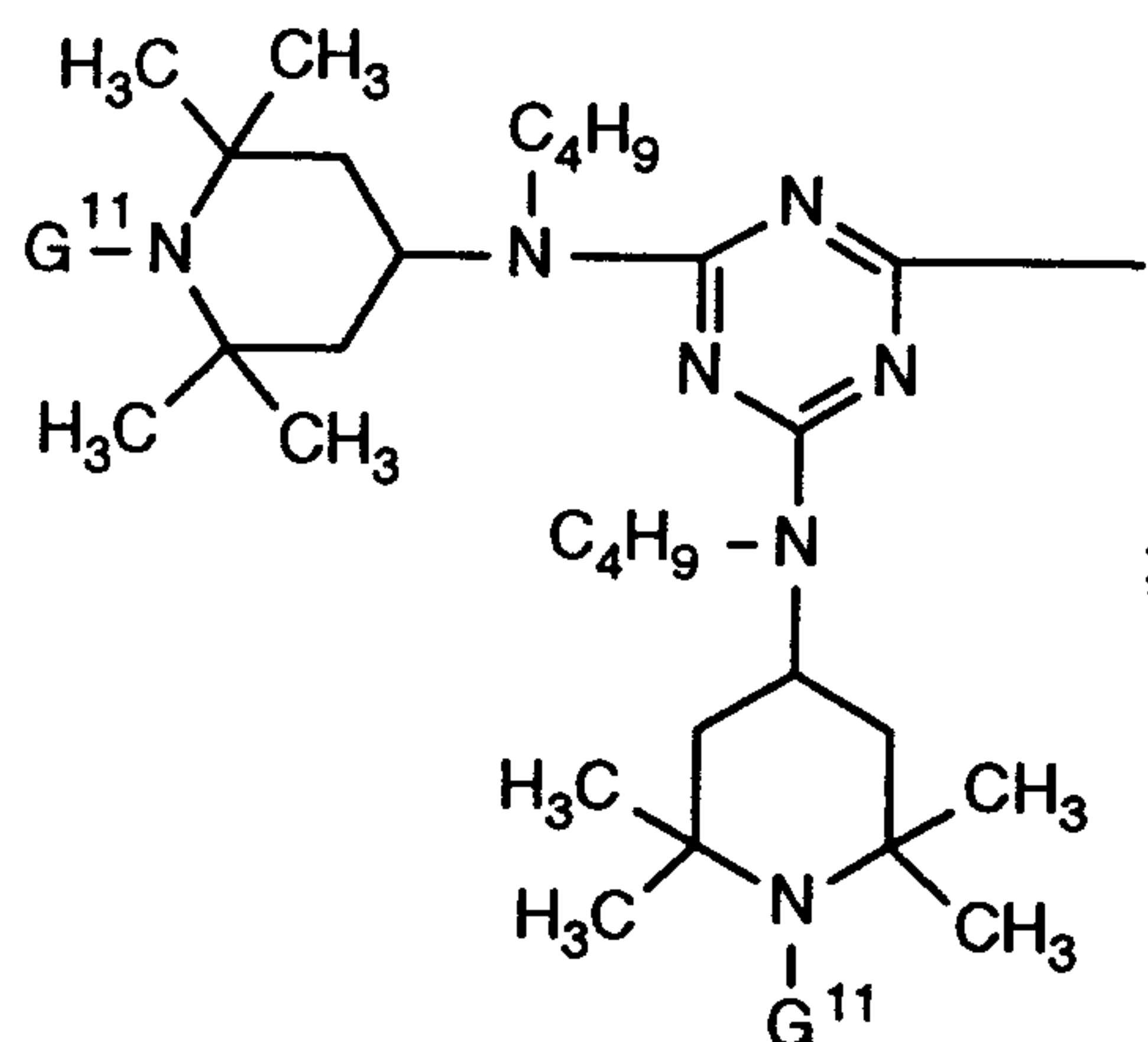
G^{20} , if $n = 1$, is identical to G^{18} and, if $n = 2$, is an $-E-B-E-$ group, in which B is

C_2 - C_8 alkylene or C_2 - C_8 alkylene which is interrupted by 1 or 2 $-N(G^{21})-$ groups,

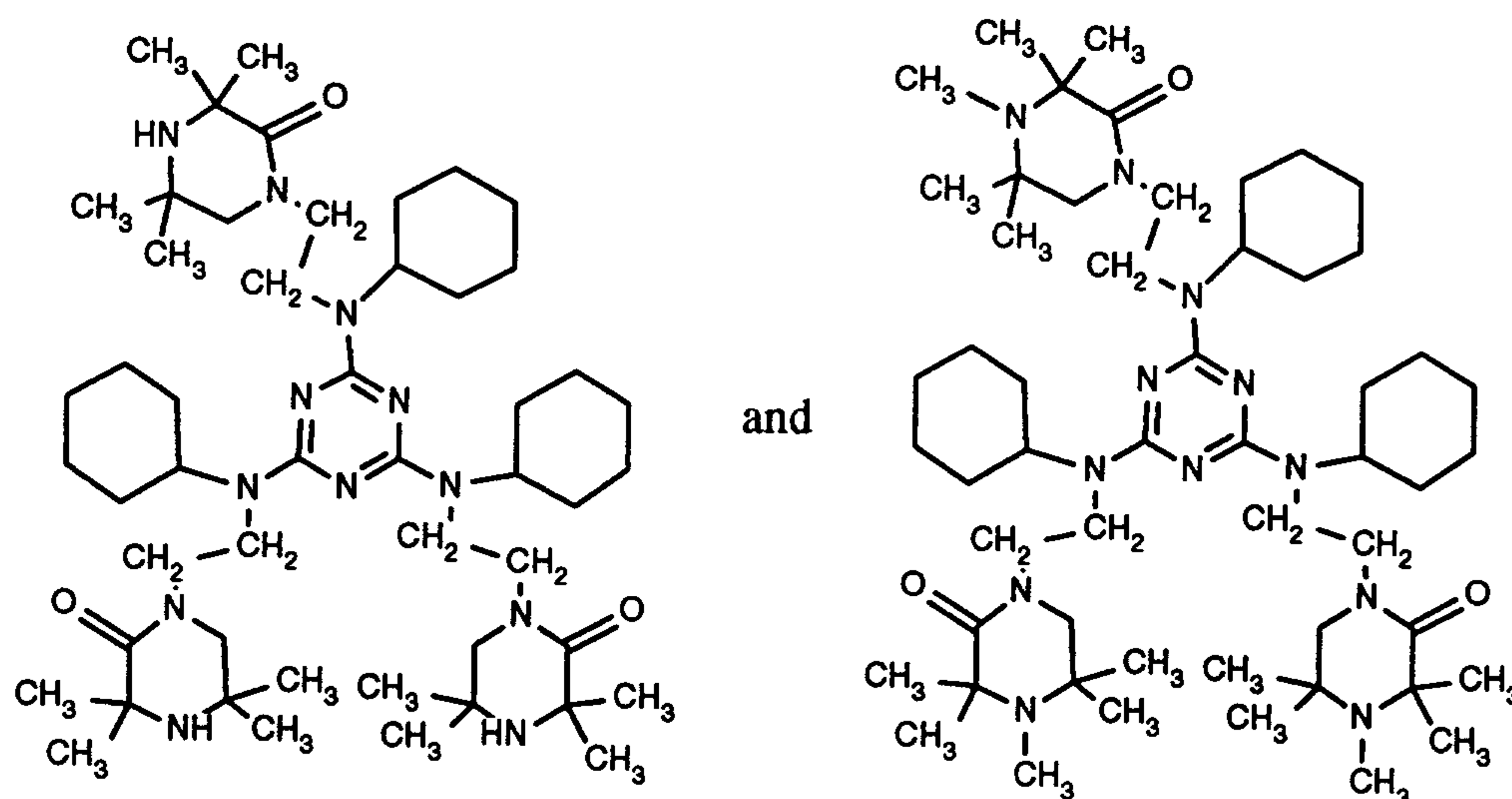
G^{21} is C_1 - C_{12} alkyl, cyclohexyl, benzyl or C_1 - C_4 hydroxyalkyl or a group of the formula



or G^{21} is a group of the formula



sterically hindered amines of particular industrial interest from this class are the above-described compound (76) [= amine J] and compounds of the formulae

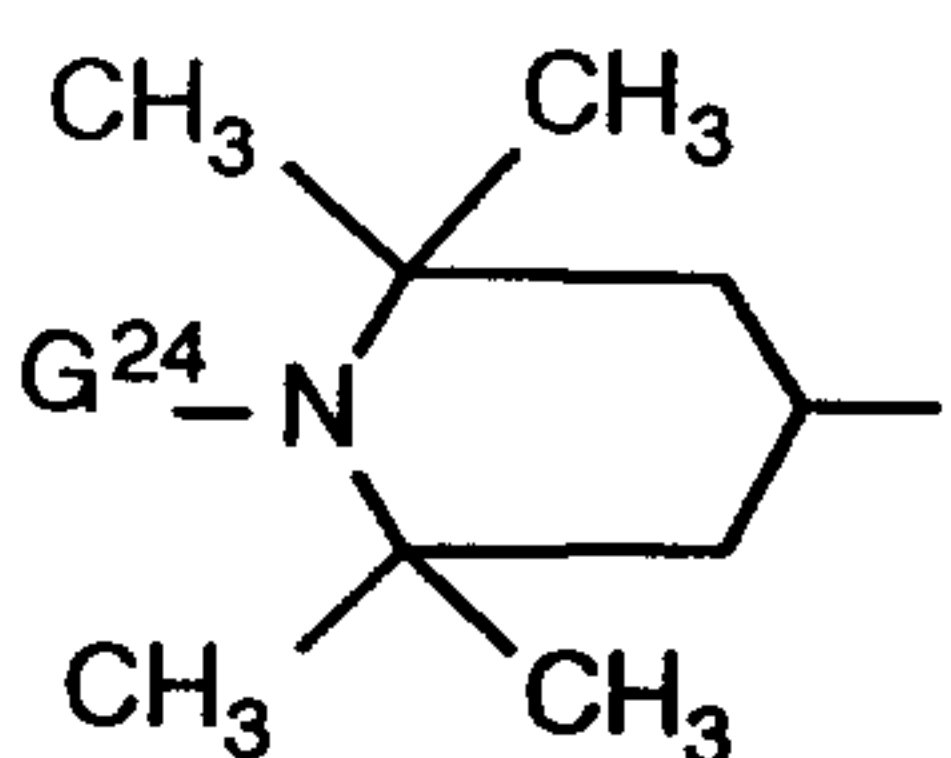


(amines K and L);

compounds of the formula X' , in which n is 2, G^{11} is hydrogen or methyl and G^{14} is C_2 - C_{12} alkylene;

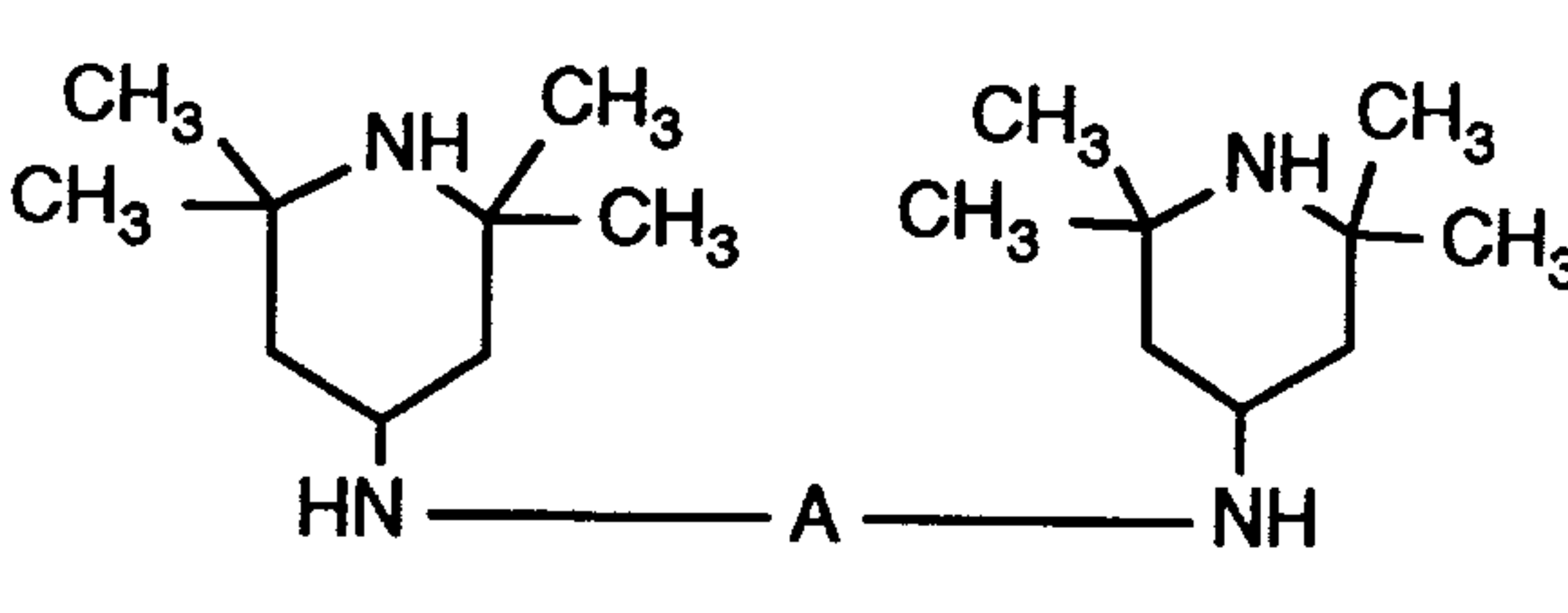
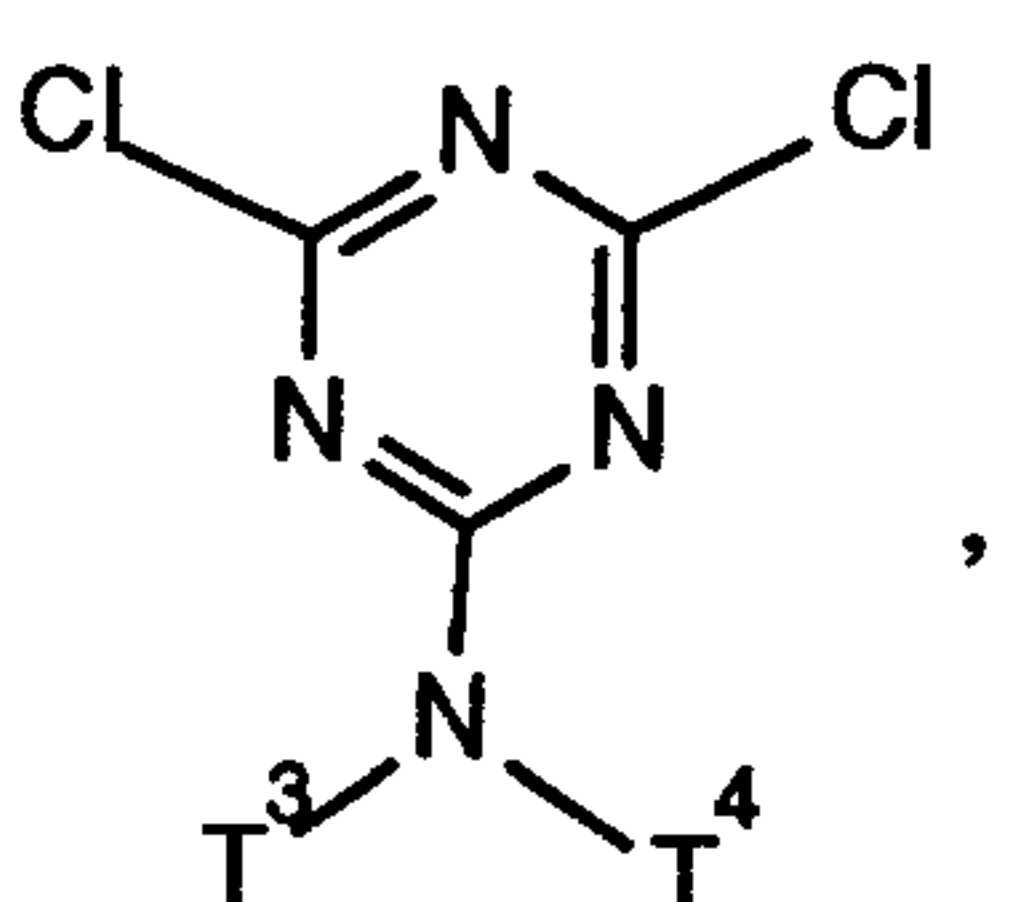
an amine of particular industrial interest from this class is the above-described compound (100)[= amine M]; and

oligomeric compounds containing 2 to 10 recurring units obtainable by reaction

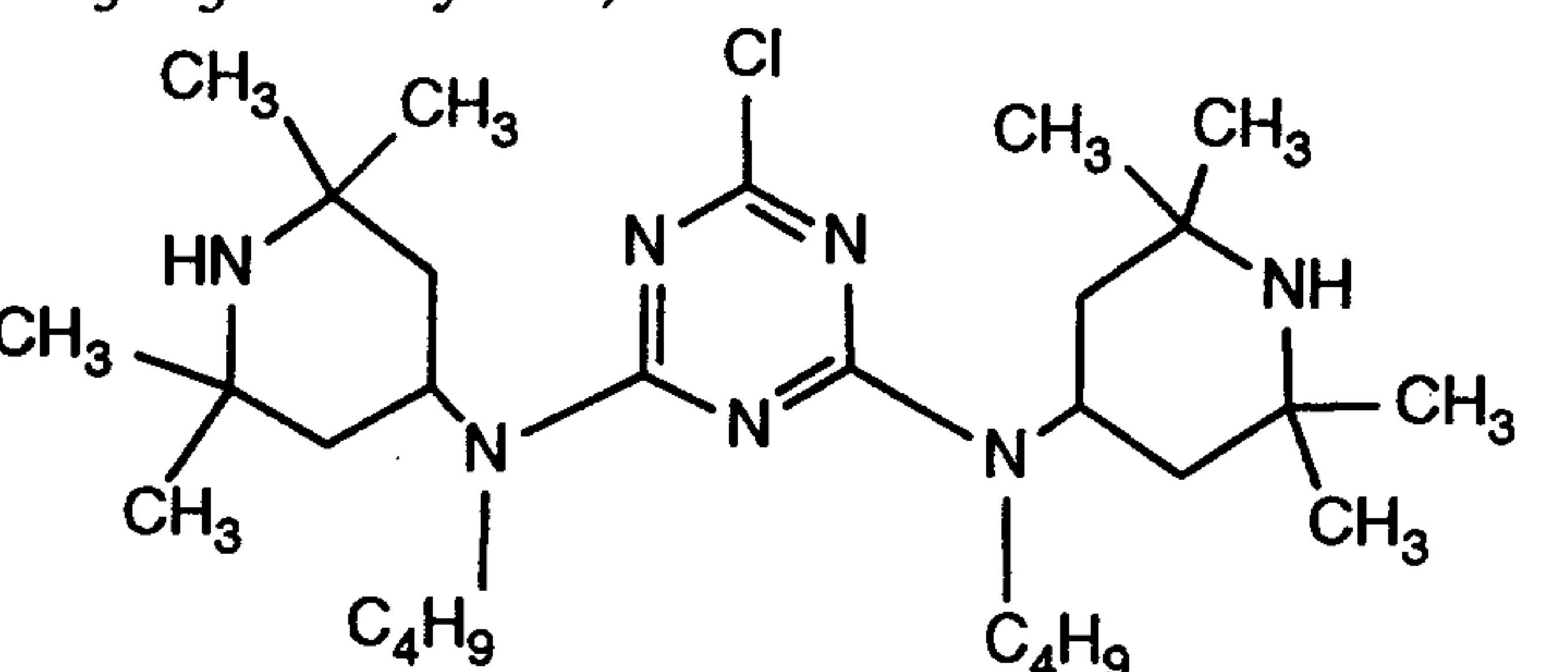
(i') of , in which G^{24} is C_2 - C_5 hydroxyalkyl, with an aliphatic

C_2 - C_{12} dicarboxylic acid or a suitable reactive derivate such as a diester, the dichloride or the anhydride;

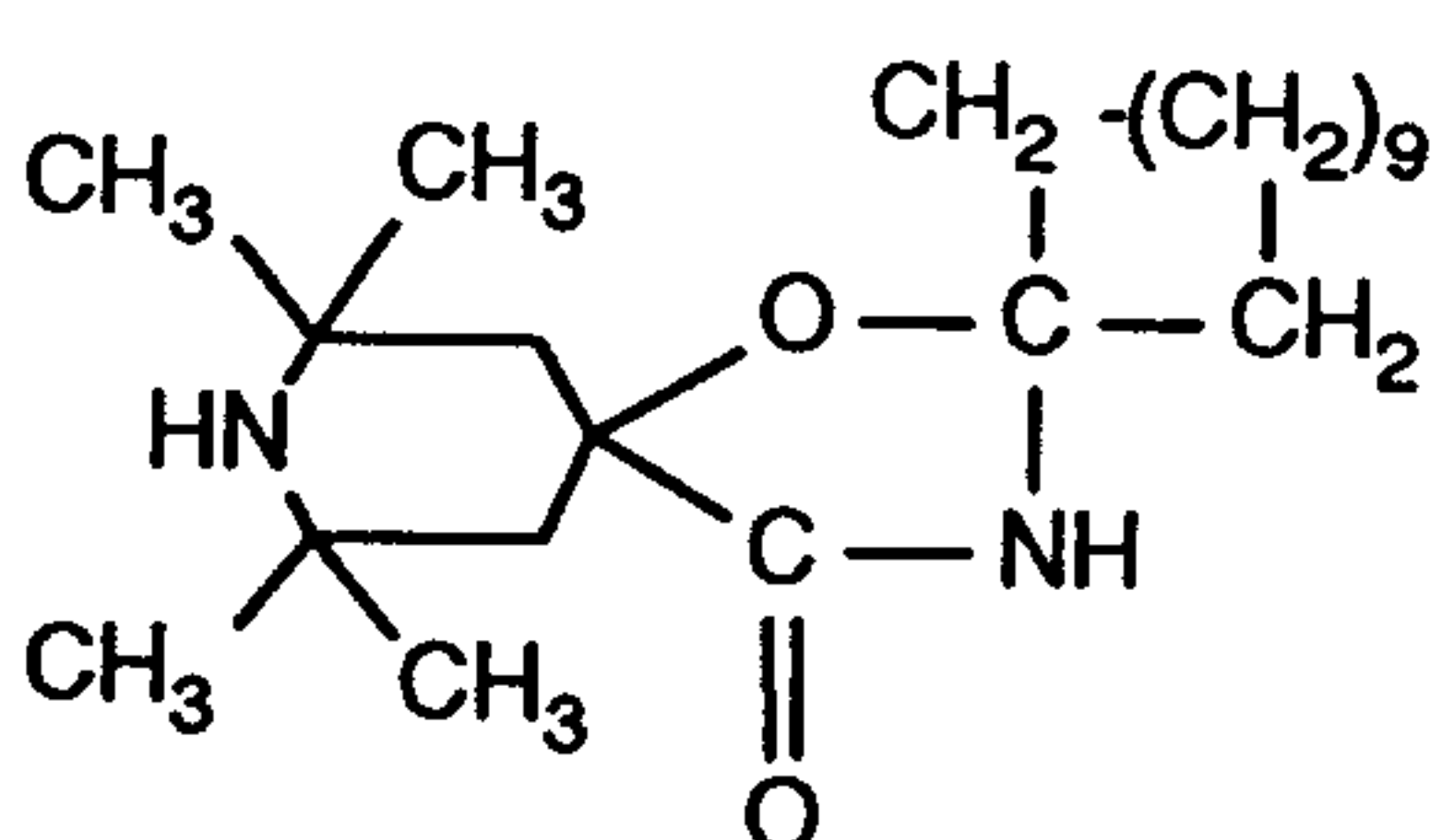
(j') of a linear oligomeric polyester made from a dialcohol and butane-1,2,3,4-tetra-carboxylic acid with 2,2,6,6-tetramethyl-4-hydroxy-piperidine;

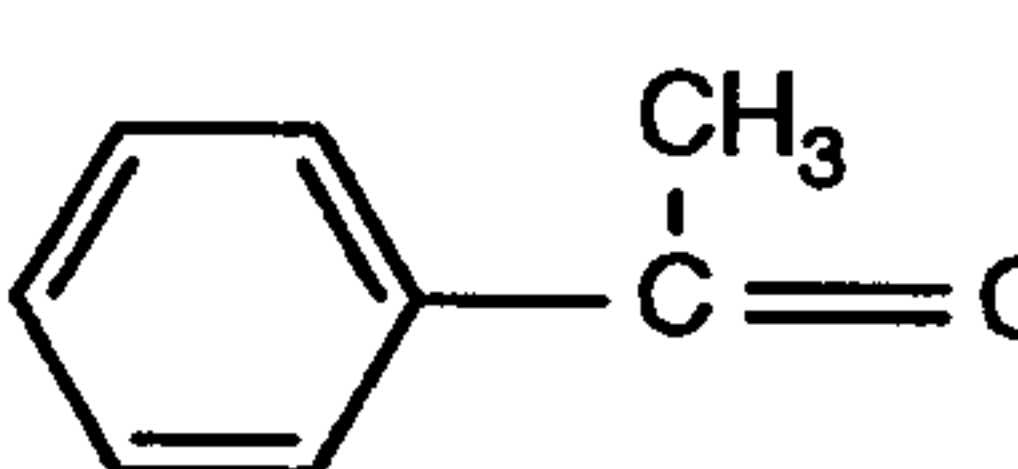
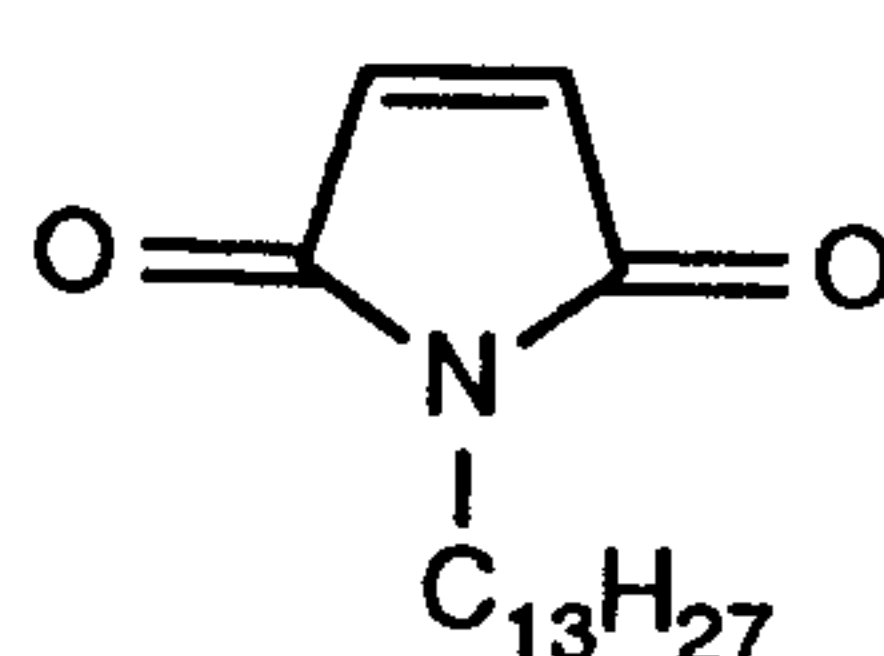
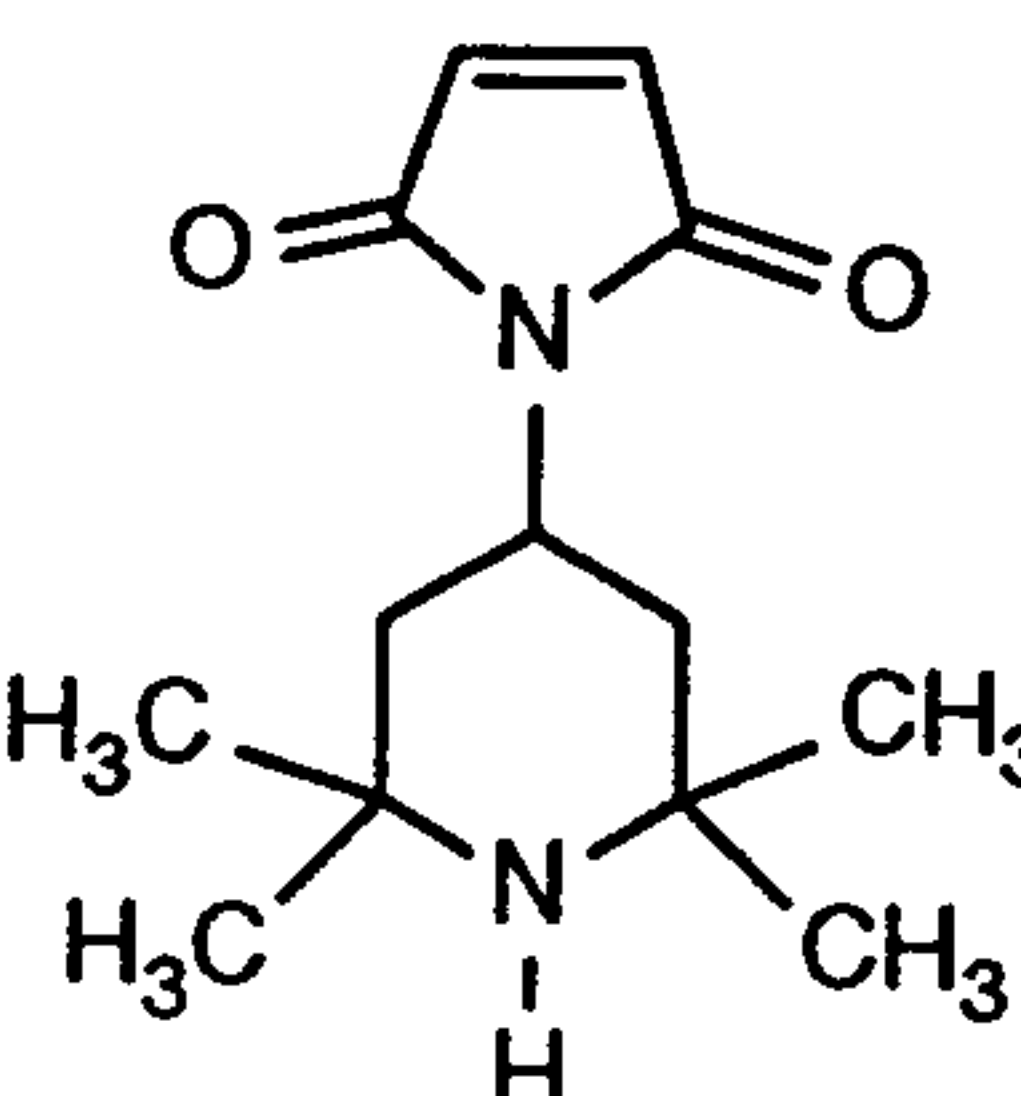
(k') of  with , in which A is

C_2 - C_6 alkylene, T^3 is C_1 - C_{18} alkyl or cyclohexyl, T^4 is hydrogen or C_1 - C_{18} alkyl, or T^3 and T^4 together are C_4 - C_6 alkylene or C_3 - C_5 oxaalkylene;

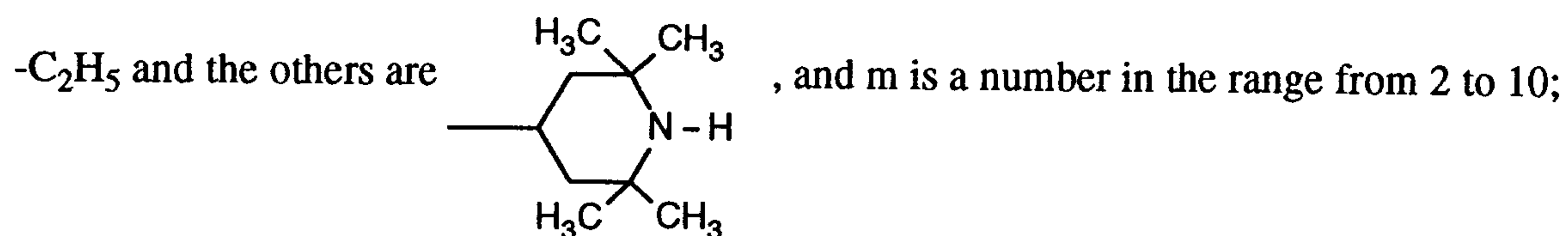
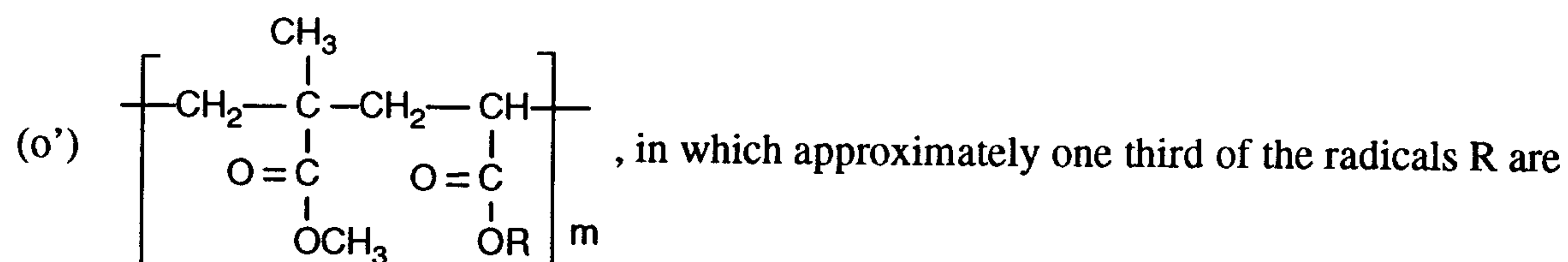
(l') of $H_2N-A-NH-A-NH_2$ with  and

$Br-A-Br$, in which A is C_2 - C_6 alkylene;

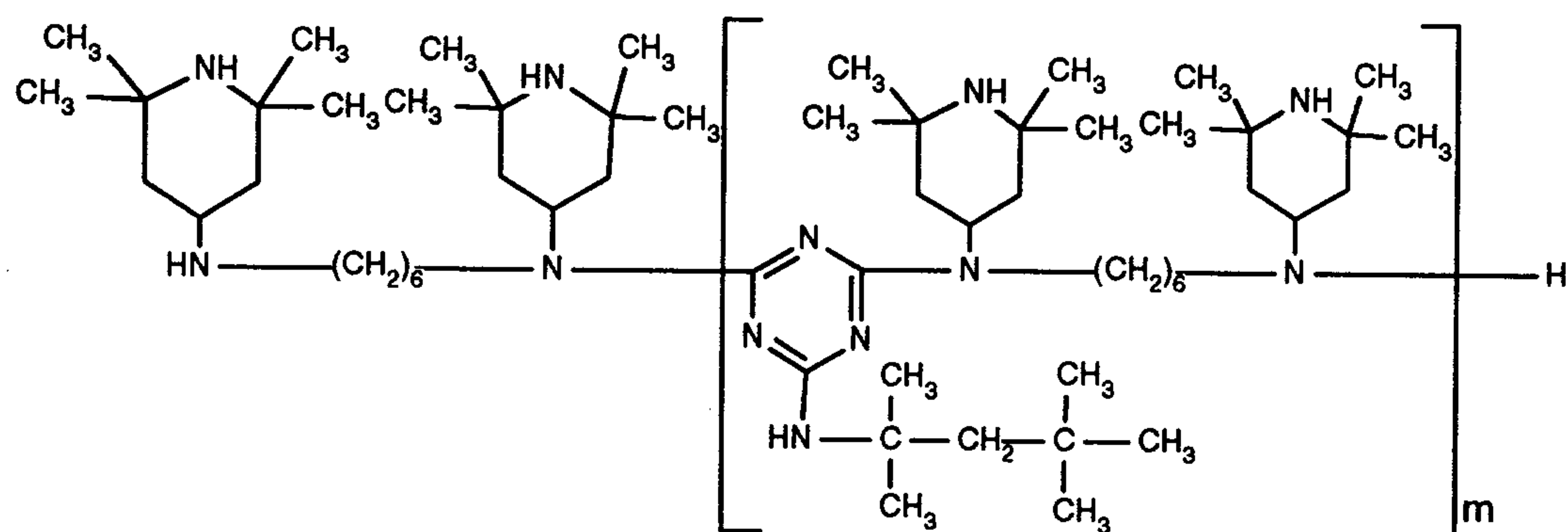
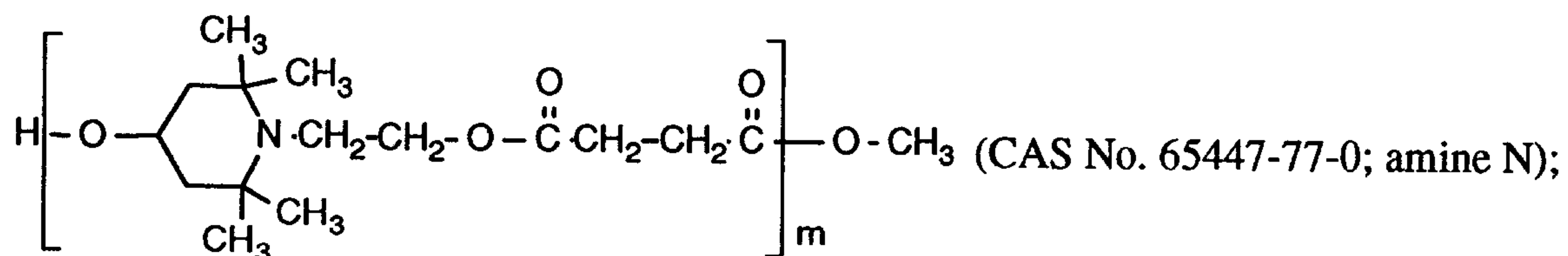
(m') of compounds of the formula  with epichlorohydrin;

(n') of  with  and ,

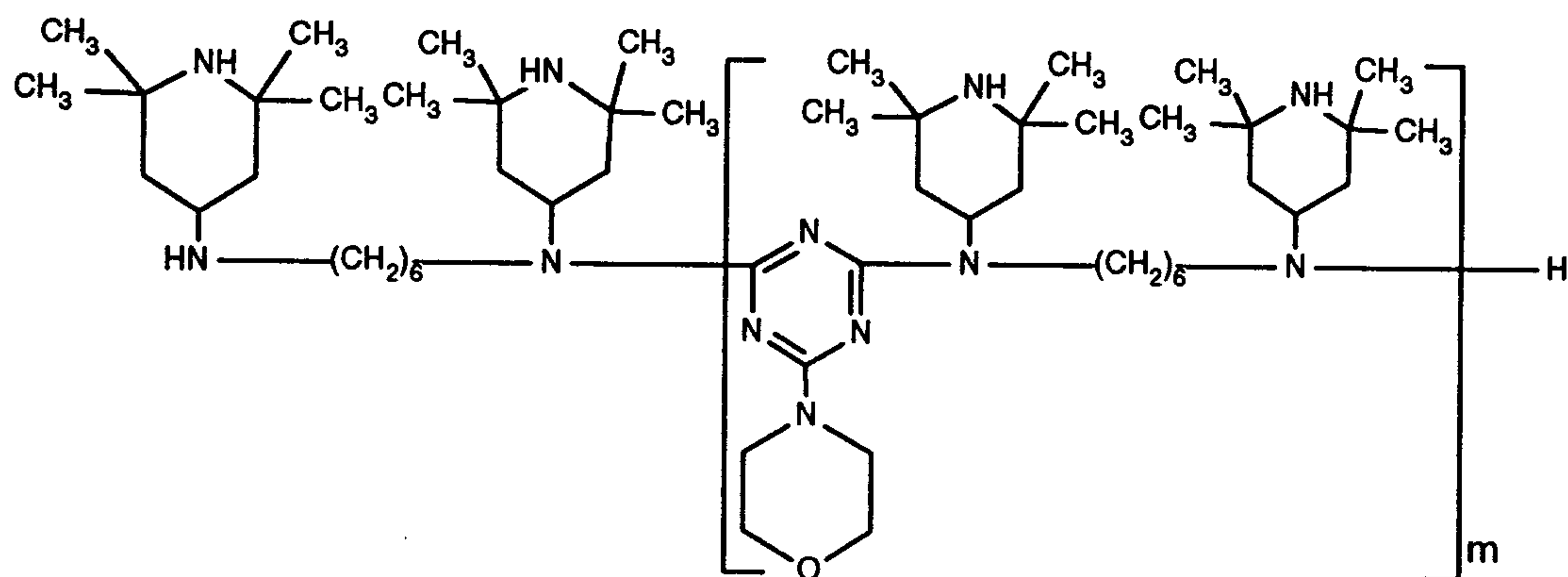
and those of the formula

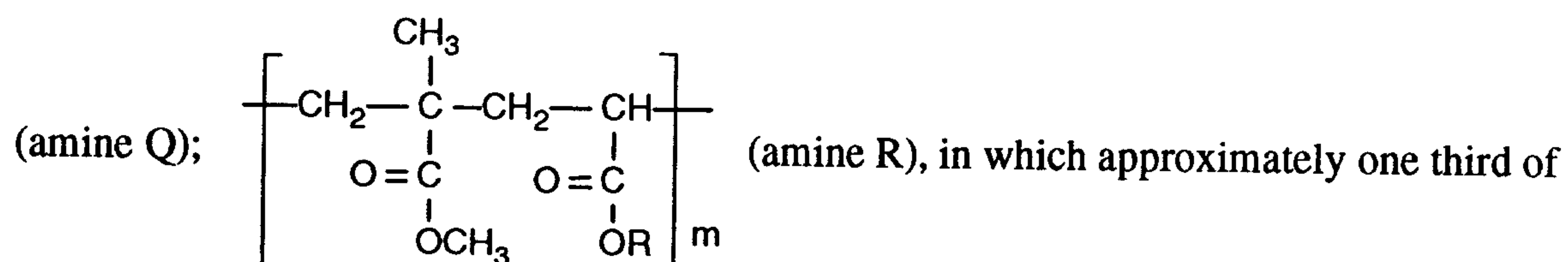


oligomeric amines of particular industrial interest also include those of the formulae (m is again a number in the range from 2 to 10)

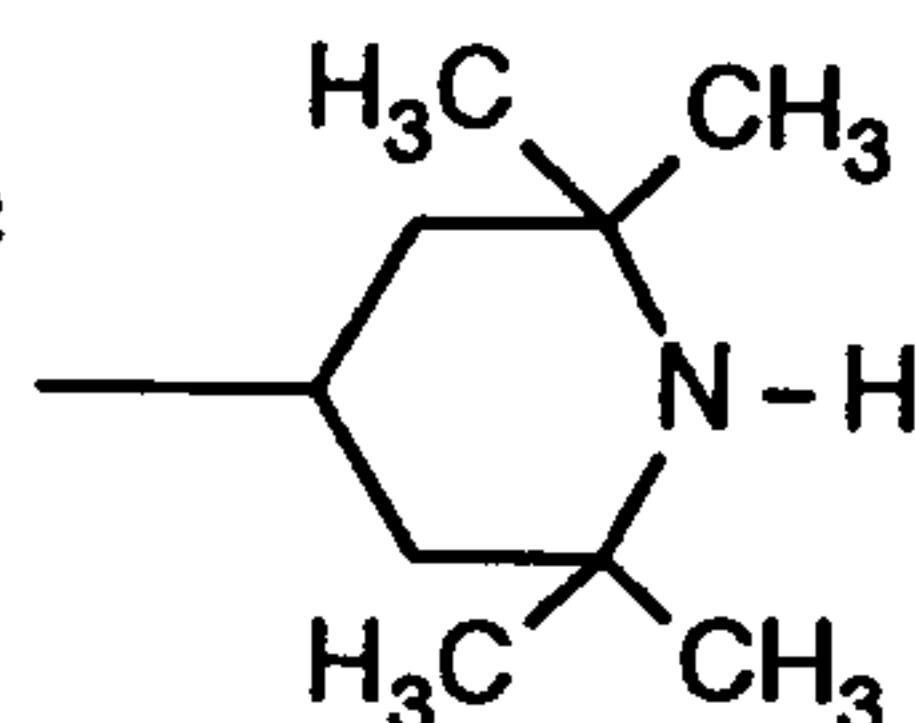


(CAS No. 70624-18-9; amine P);



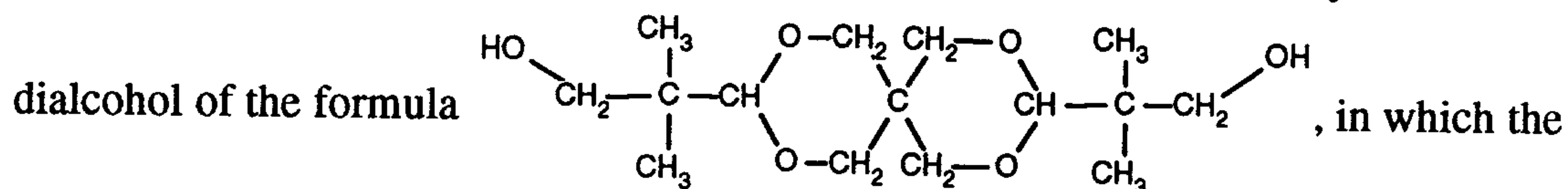


the radicals R are $-\text{C}_2\text{H}_5$ and the others are

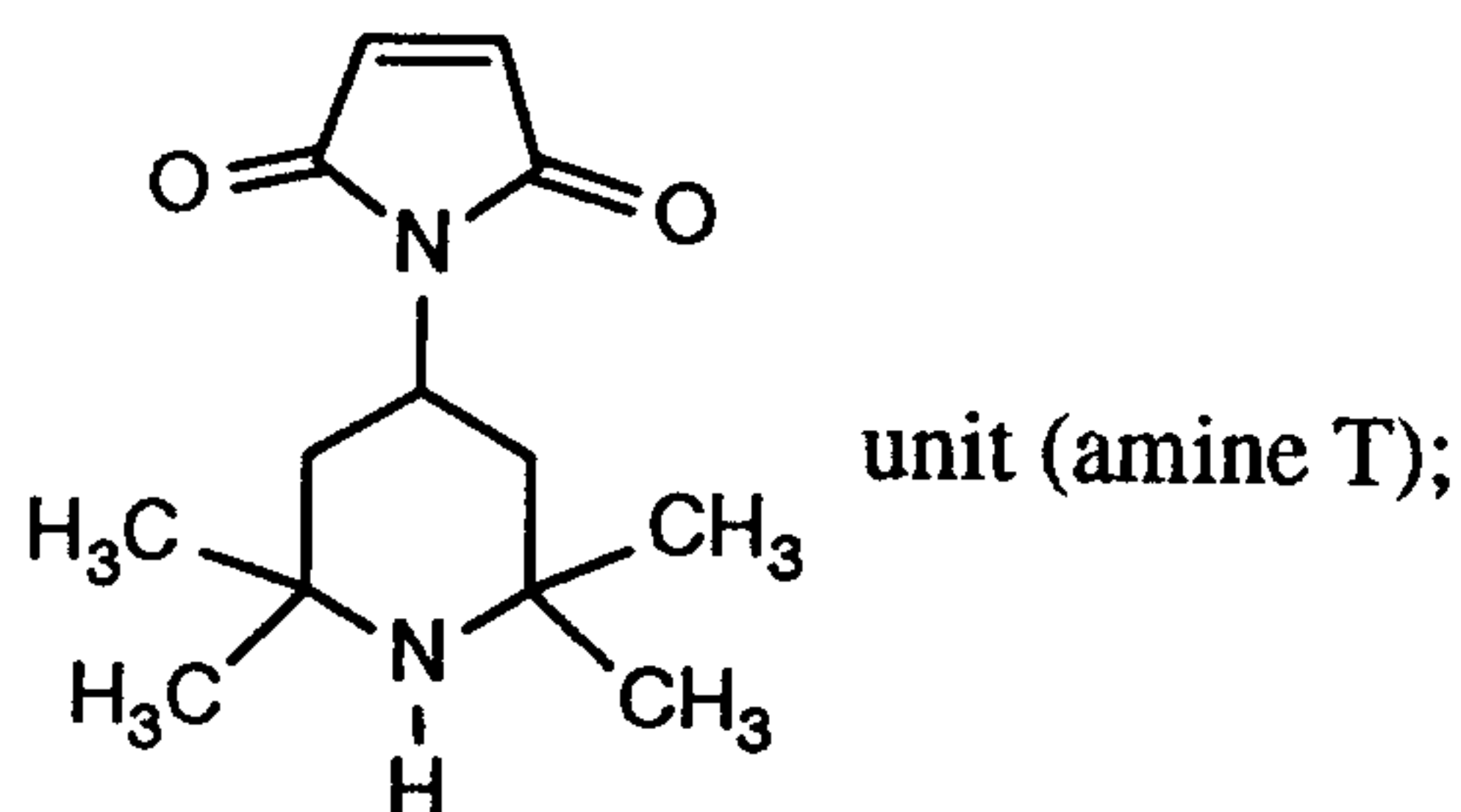
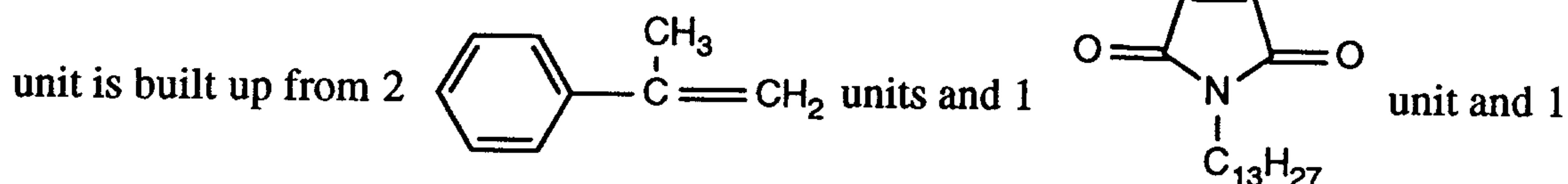


; a linear polyester

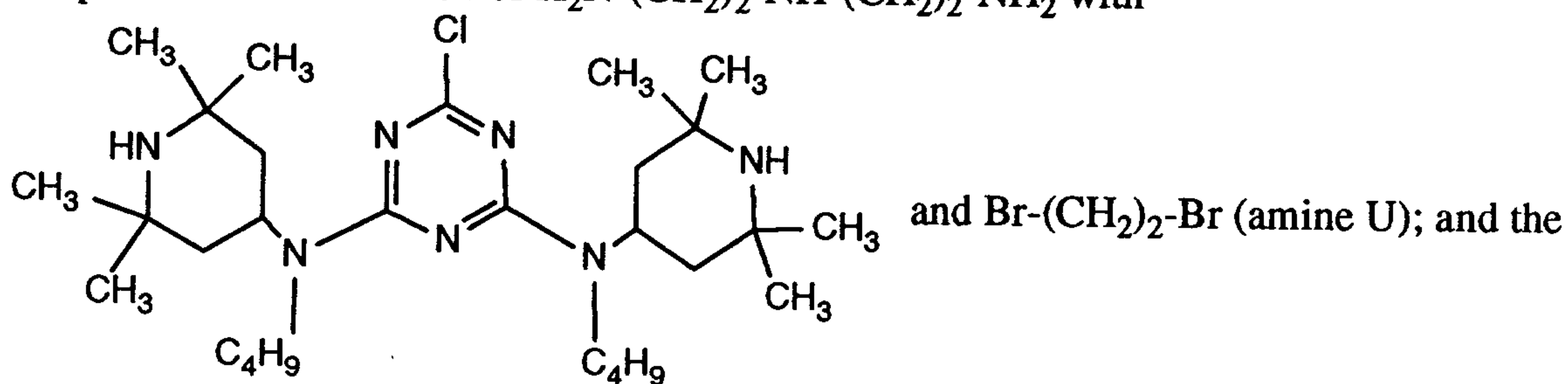
containing 2 to 10 recurring units made from butane-1,2,3,4-tetracarboxylic acid and a



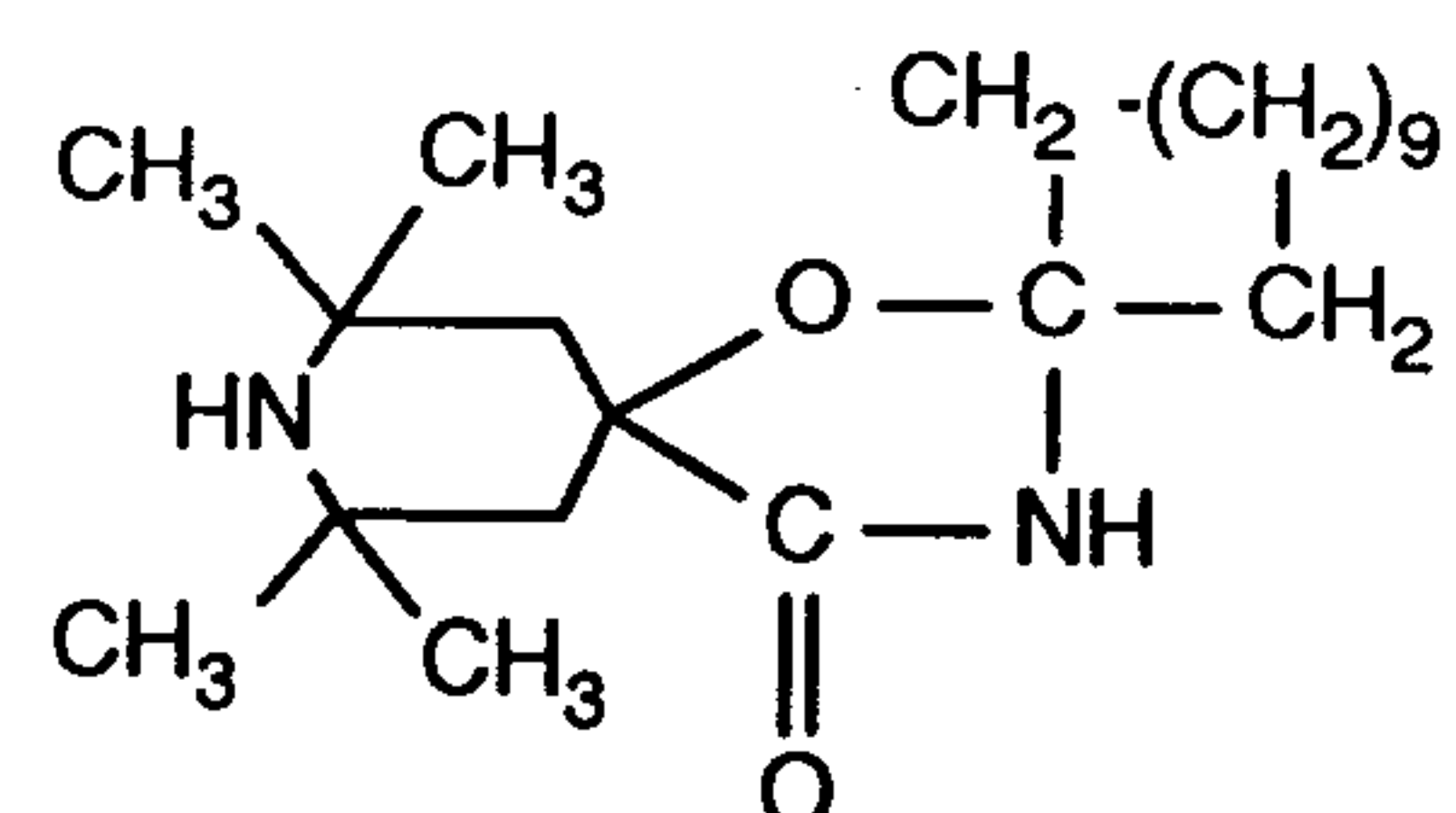
terminal groups and side chains are formed by esterification of the free carboxyl groups using 2,2,6,6-tetramethyl-4-hydroxypiperidine (amine S); a copolymer whose recurring



the product of the reaction of $\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$ with



product of the reaction of the compound of the formula



with epichlorohydrin (amine W).

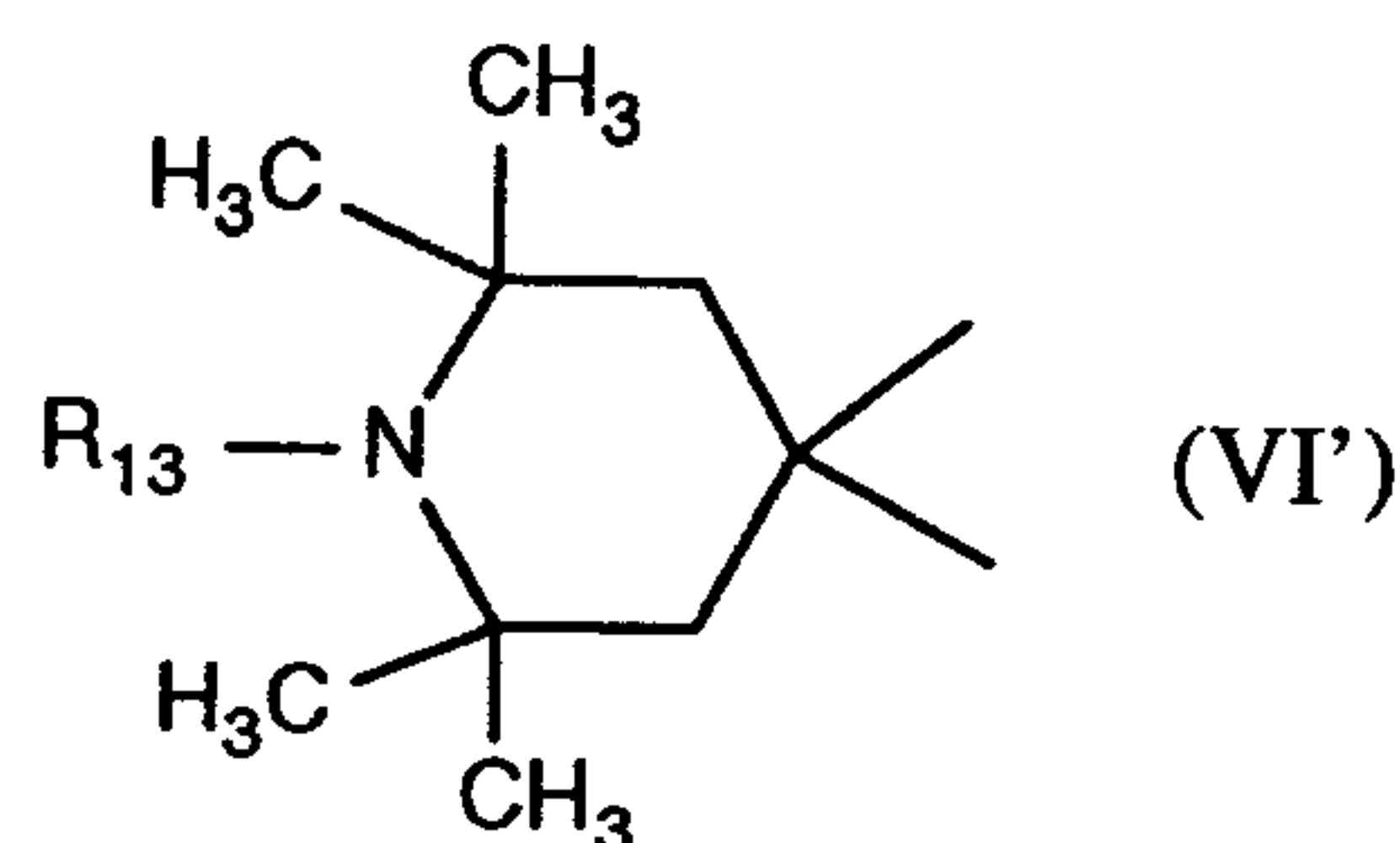
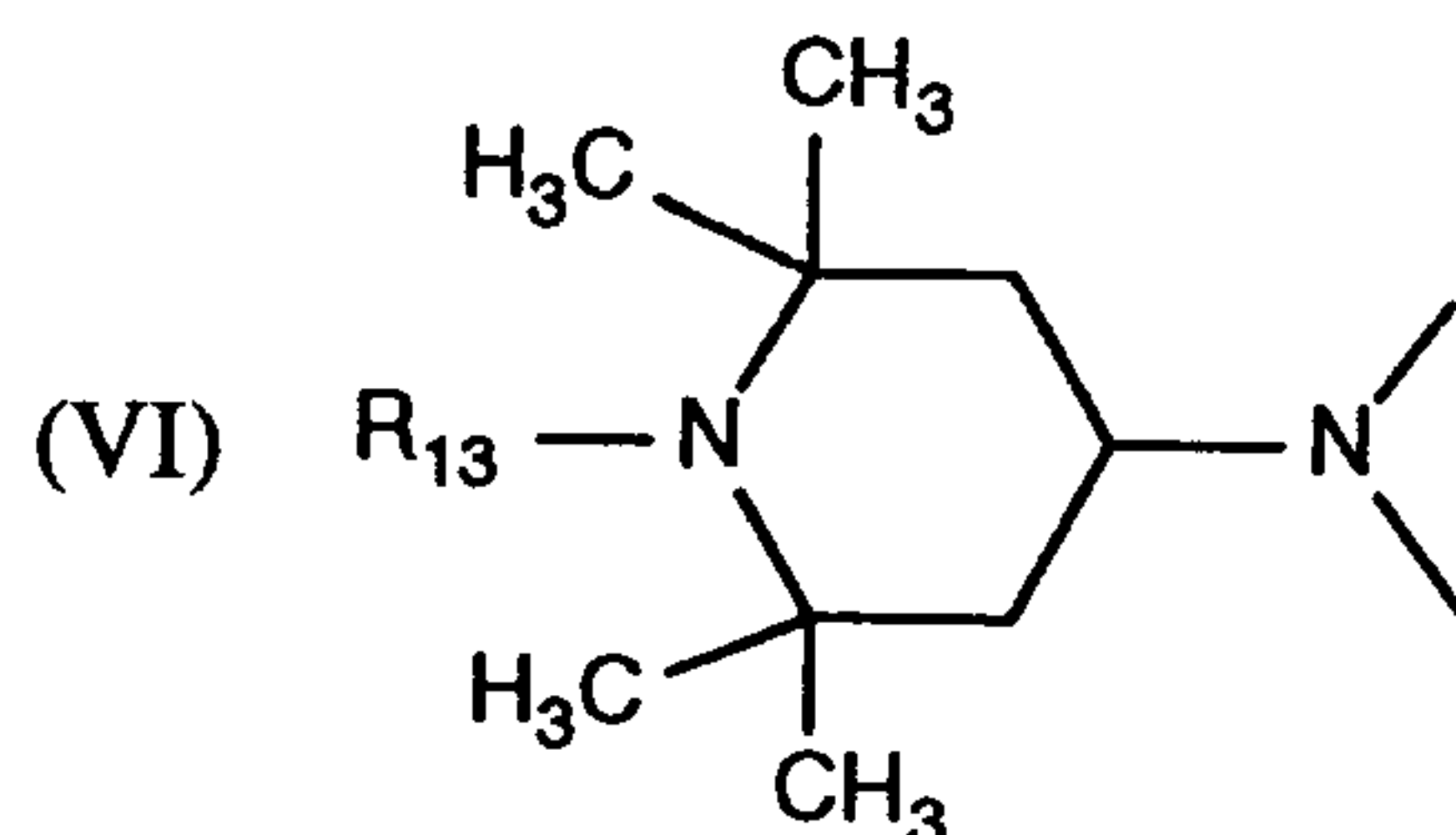
The oligomeric amines are frequently mixtures of compounds which differ from one another in chain length.

Of particular importance is the use of the above-specified amines A, B, C, D, E, F, G, H, J, K, L, M, N, O, P, Q, R, S, T, U, V and W.

For the novel compositions, particular preference is given to the addition of sterically hindered amines whose molecular weight or mean molecular weight $\bar{M}_n$ is in the range from 500 to 10,000, in particular in the range from 1000 to 10,000. Of these, particular emphasis should again be made of sterically hindered amines whose molecular weight or mean molecular weight $\bar{M}_n$ is in the range from 1500 to 10,000, for example in the range from 2000 to 7500.

Particular emphasis should be made of novel compositions in which component (c)(ii) or component (c)(iii)(y) consists of two or more compounds of the sterically hindered amine type.

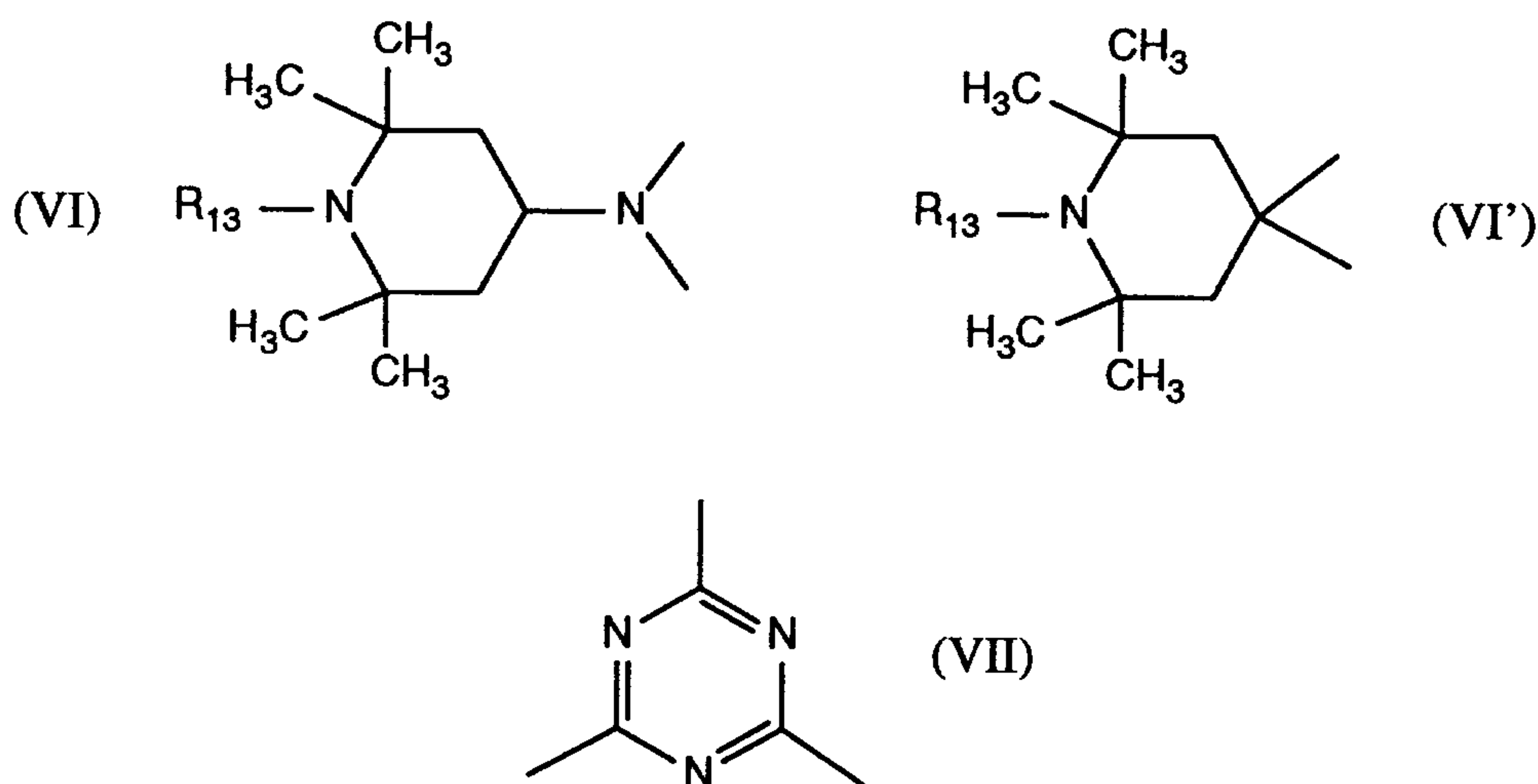
Special preference is given to compositions comprising as component (c)(ii) or component (c)(iii)(y) a compound from the group consisting of sterically hindered amines in which the molecular weight is greater than 1000 and the compound contains at least one radical of the formula VI or VI'



in which

R_{13} is hydrogen or methyl.

Very special preference is given to compositions comprising as component (c)(ii) or component (c)(iii)(y) a compound from the group of sterically hindered amines in which the molecular weight is greater than 1000 and the compound contains at least one radical of the formula VI or VI' and one radical of the formula VII



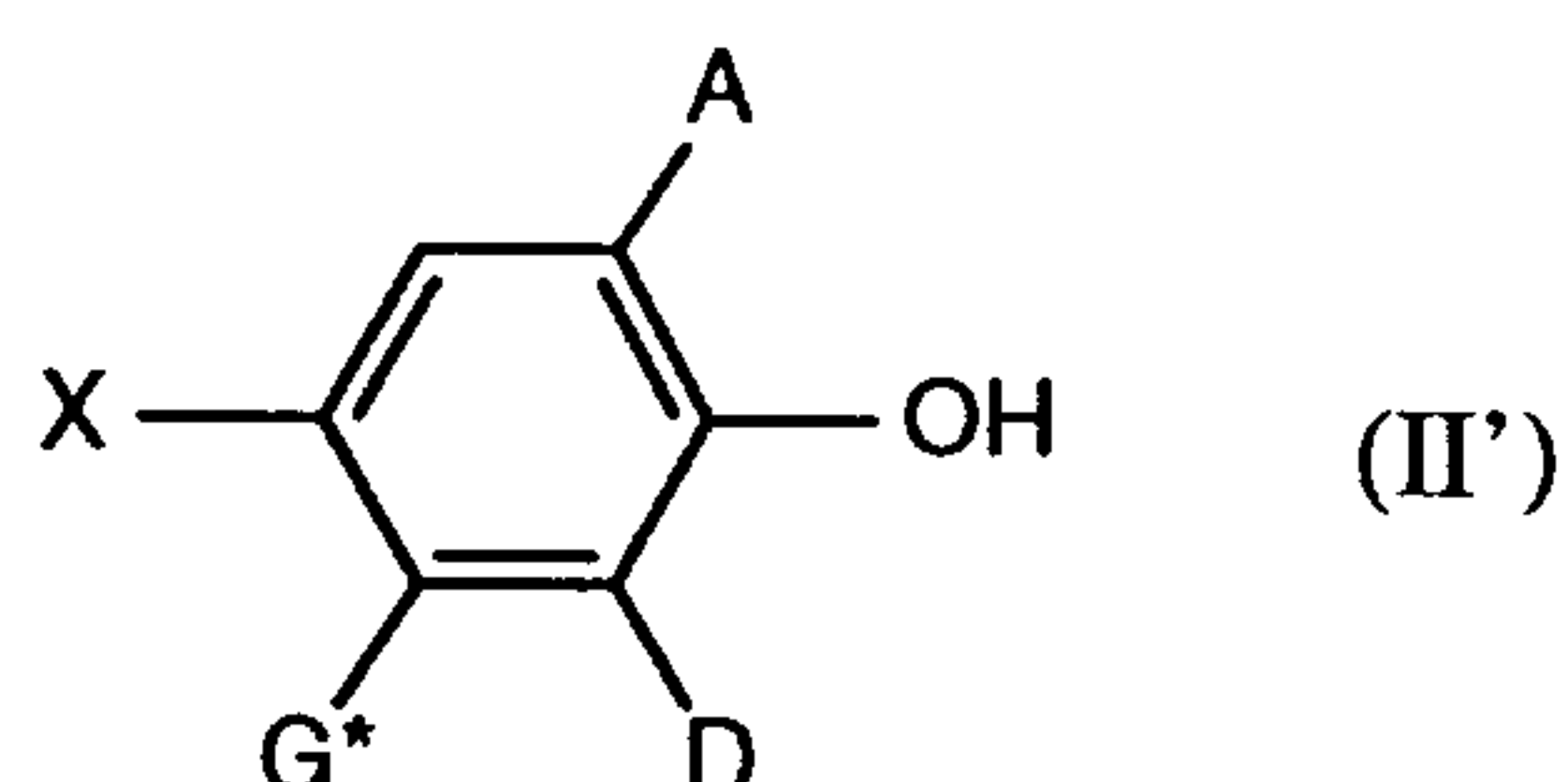
in which

R_{13} is hydrogen or methyl.

Of very particular interest are compositions comprising as component (c)(ii) or component (c)(iii)(y) a linear or cyclic condensation product prepared from N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine [Chimassorb[®] 944LD (Ciba-Geigy), amine P in the above description]; or a condensation product prepared from 2-chloro-4,6-di(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane [Chimassorb[®] 119FL/10 (Ciba-Geigy), compound No. 76].

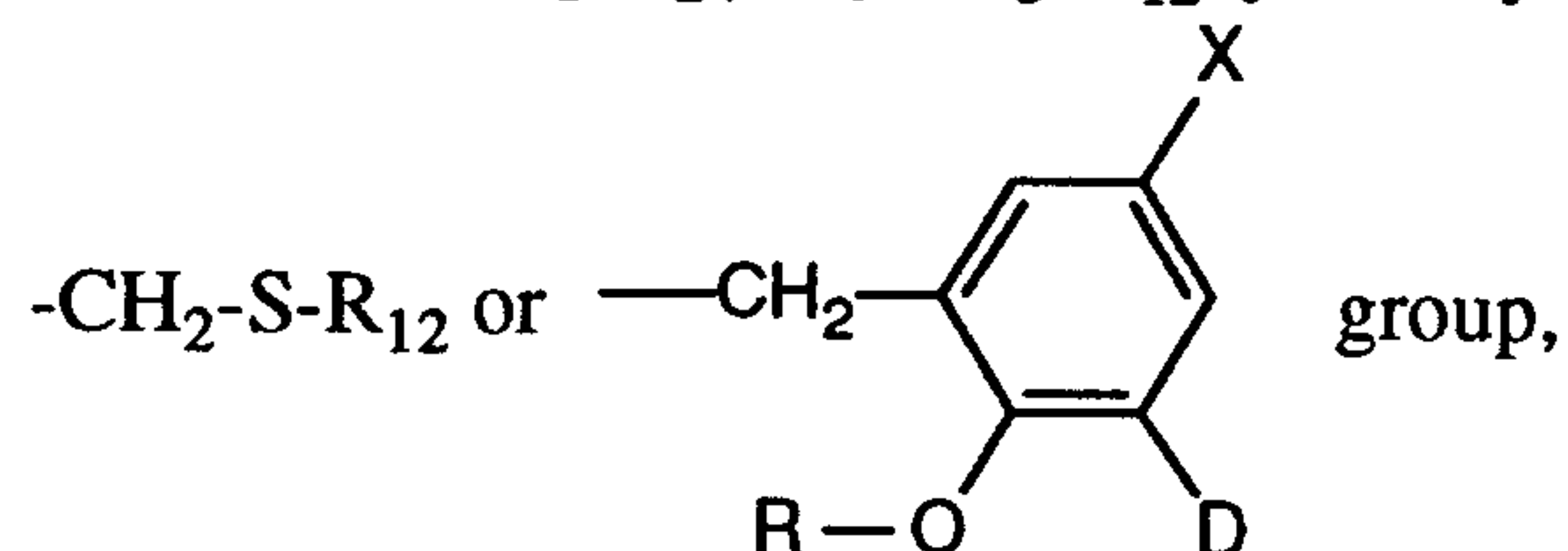
The sterically hindered amines mentioned are known compounds, and many of them are commercially available.

Of interest are compositions comprising as component (c)(iii)(x) a phenolic antioxidant of the formula II'



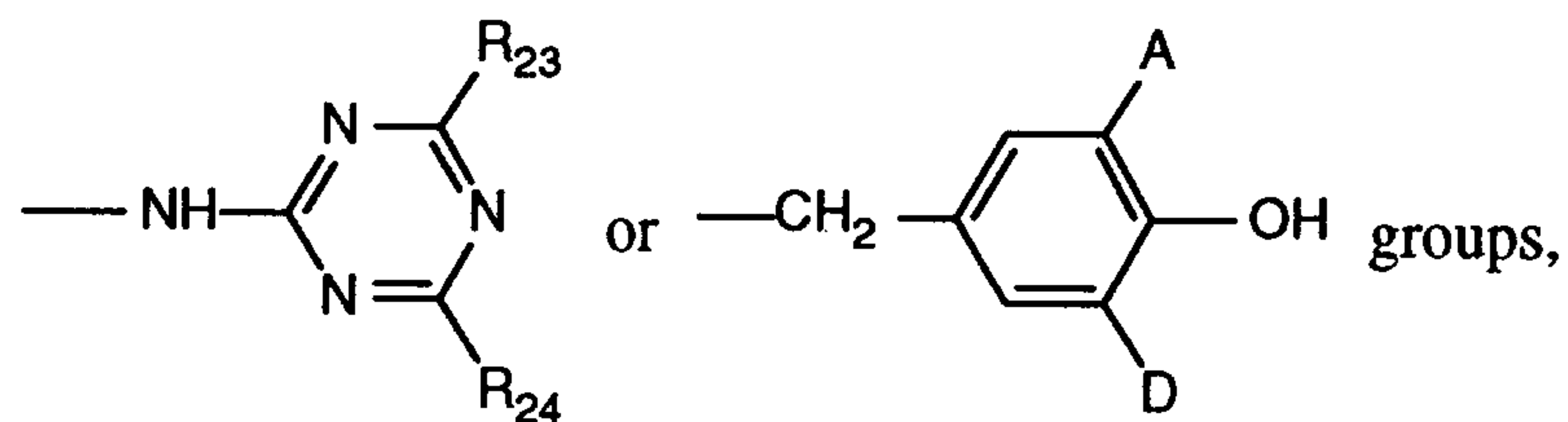
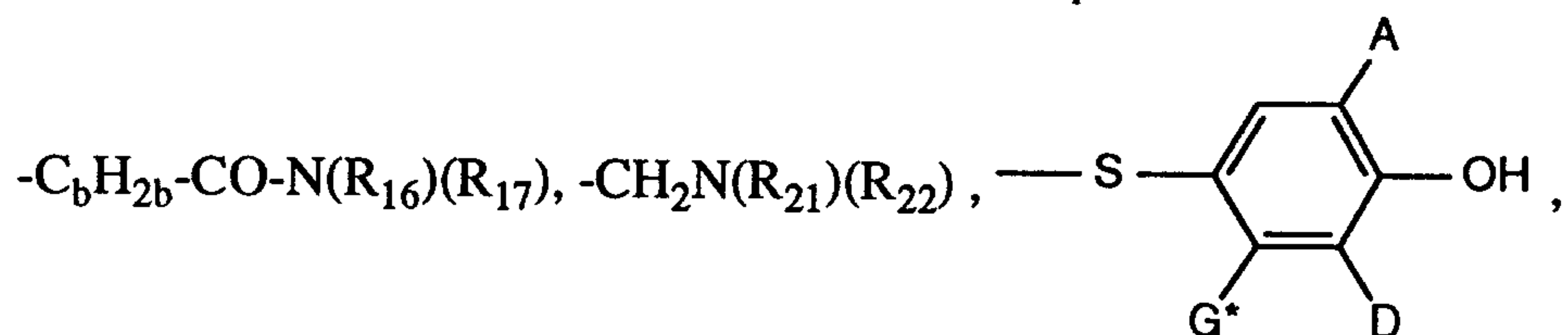
in which

A is hydrogen, C₁-C₂₄alkyl, C₅-C₁₂cycloalkyl, phenyl-C₁-C₄alkyl, phenyl or a



D is C₁-C₂₄alkyl, C₅-C₁₂cycloalkyl, phenyl-C₁-C₄alkyl, phenyl or a -CH₂-S-R₁₂ group,

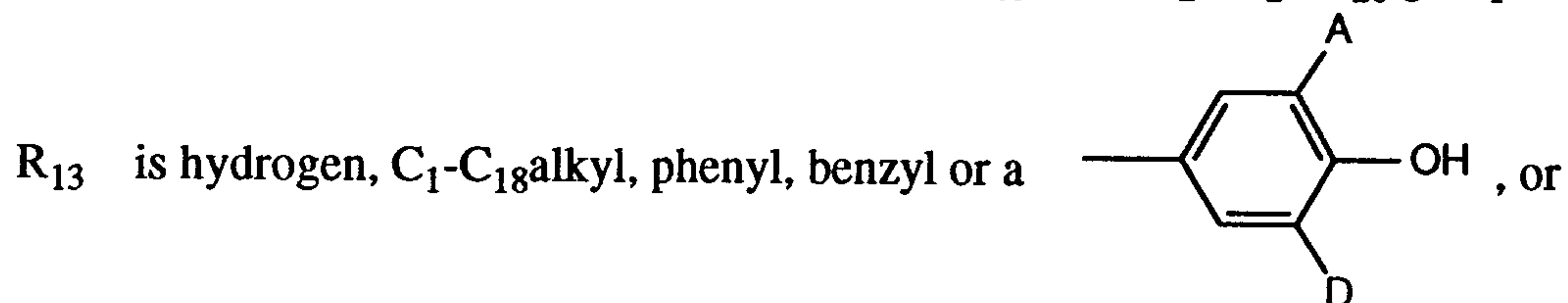
X is hydrogen, C₁-C₁₈alkyl or one of the -C_aH_{2a}-S_q-R₁₃, -C_bH_{2b}-CO-OR₁₄,



R is hydrogen or a group of the formula -CO-CH=CH₂,

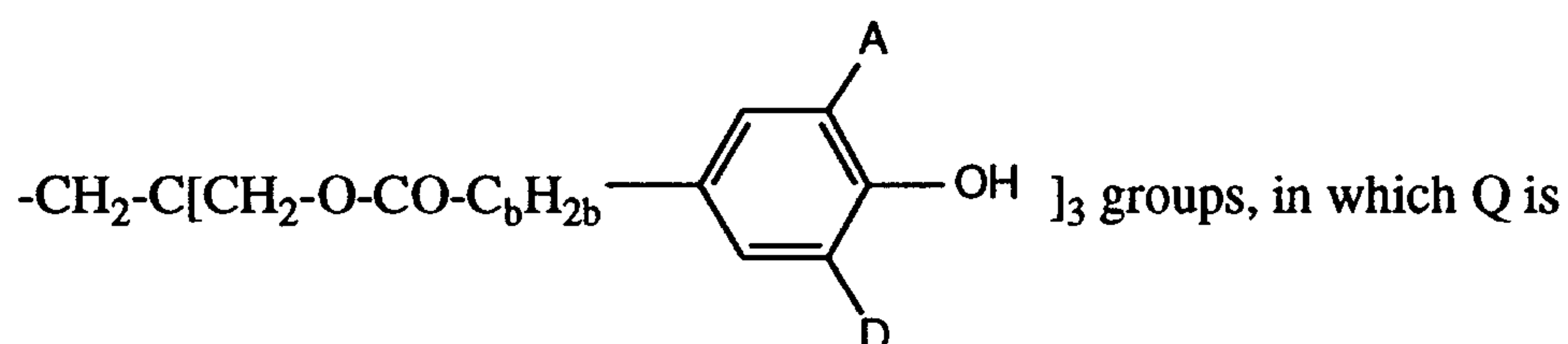
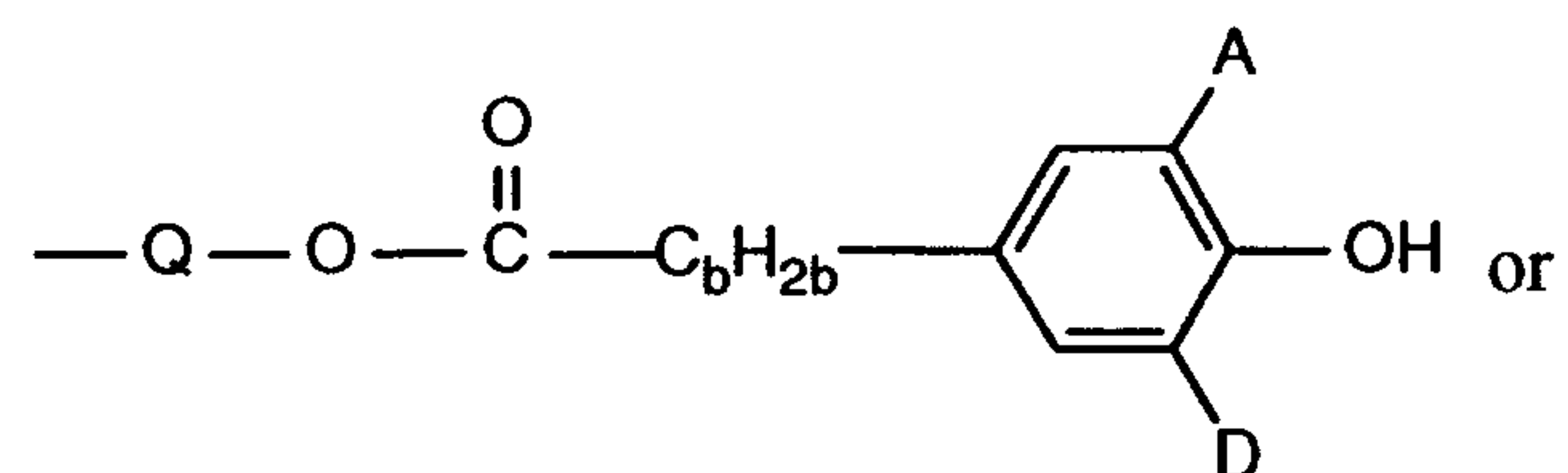
G* is hydrogen or C₁-C₁₂alkyl,

R₁₂ is C₁-C₁₈alkyl, phenyl or a -(CH₂)_c-CO-OR₁₅ or -CH₂CH₂OR₂₀ group,



-(CH₂)_c-CO-OR₁₅ or -CH₂-CH₂-OR₂₀ group,

R₁₄ is C₁-C₃₀alkyl or one of the -CHR₁₈-CH₂-S-R₁₉,

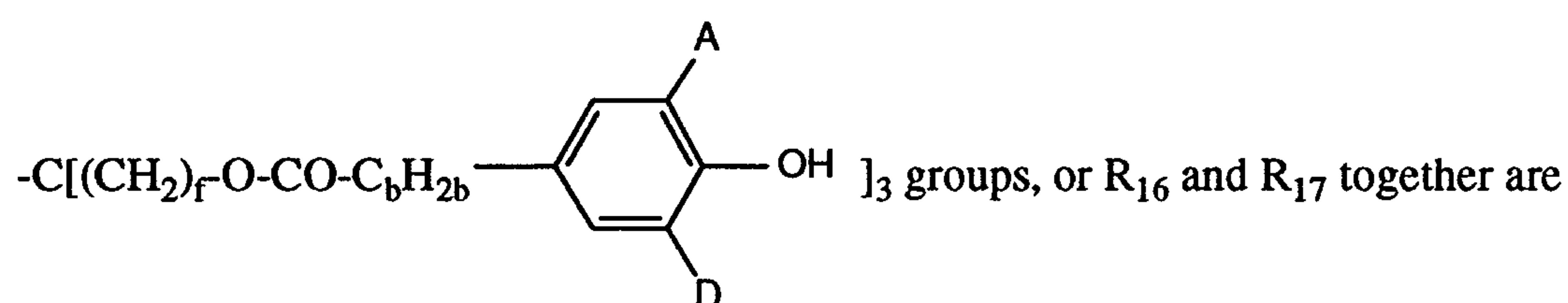
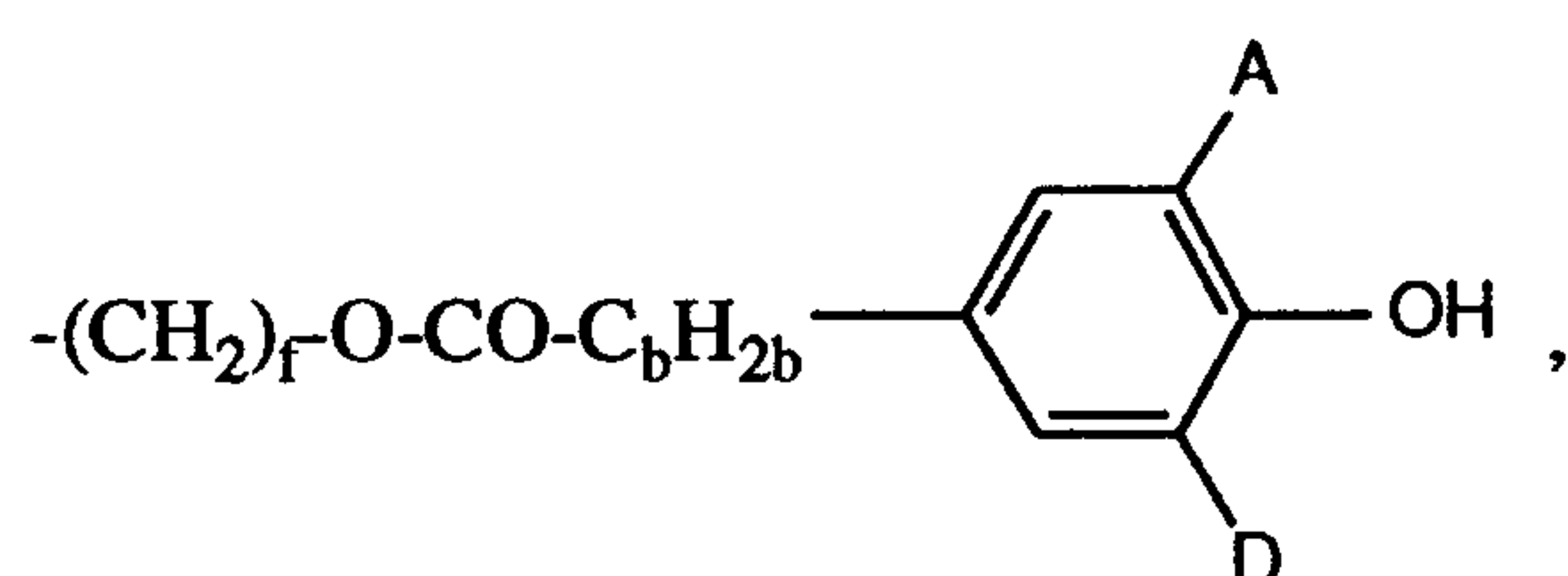
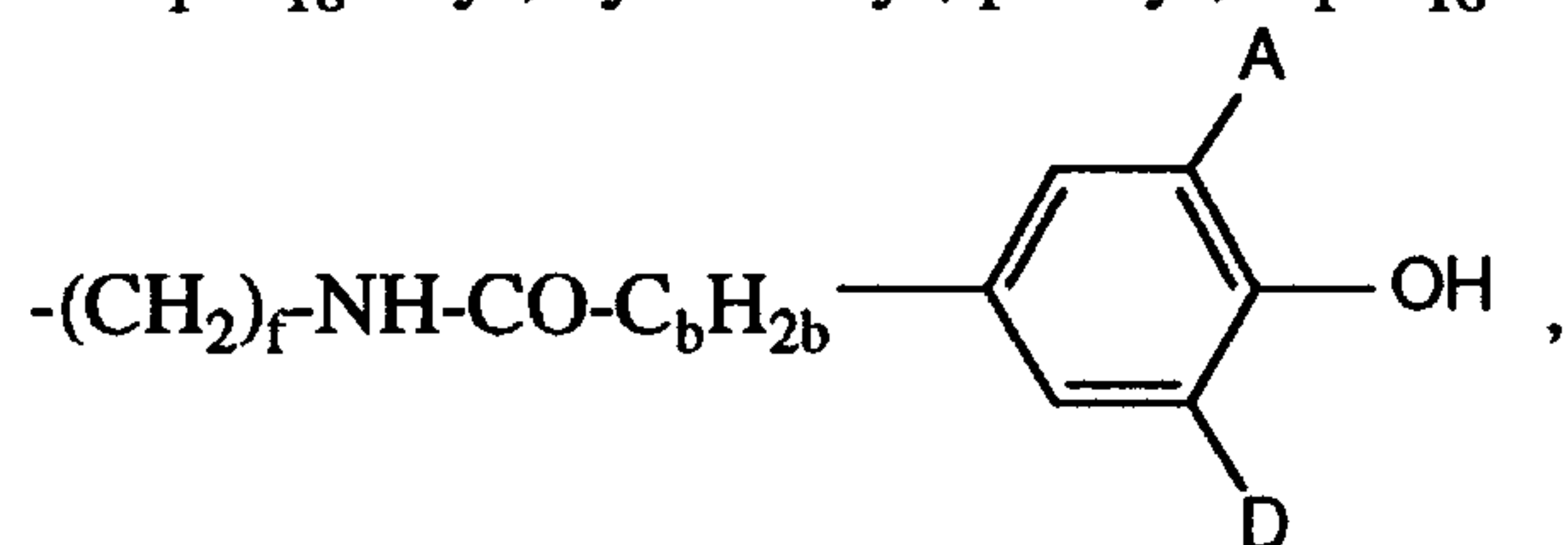


C_2 - C_8 alkylene, C_4 - C_6 thiaalkylene or a $-CH_2CH_2(OCH_2CH_2)_d-$ group,

R_{15} is C_1 - C_{24} alkyl,

R_{16} is hydrogen, C_1 - C_{18} alkyl or cyclohexyl,

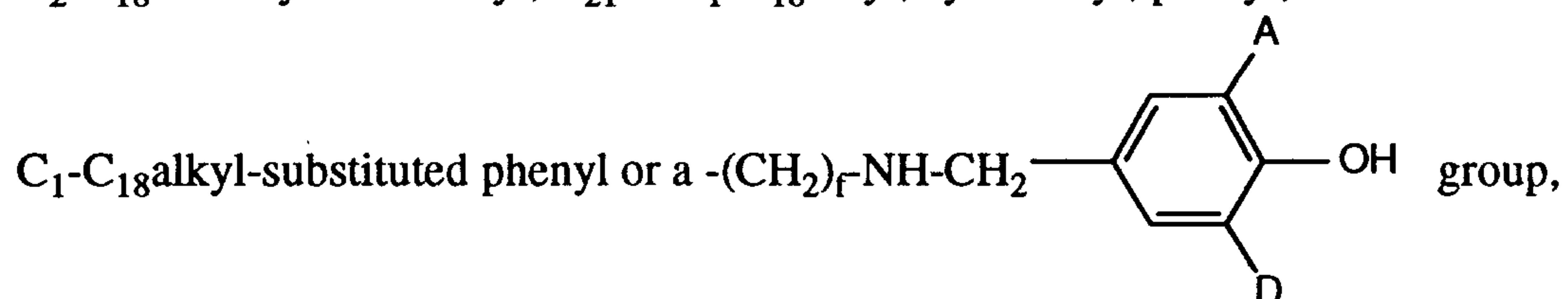
R_{17} is C_1 - C_{18} alkyl, cyclohexyl, phenyl, C_1 - C_{18} alkyl-substituted phenyl or one of the

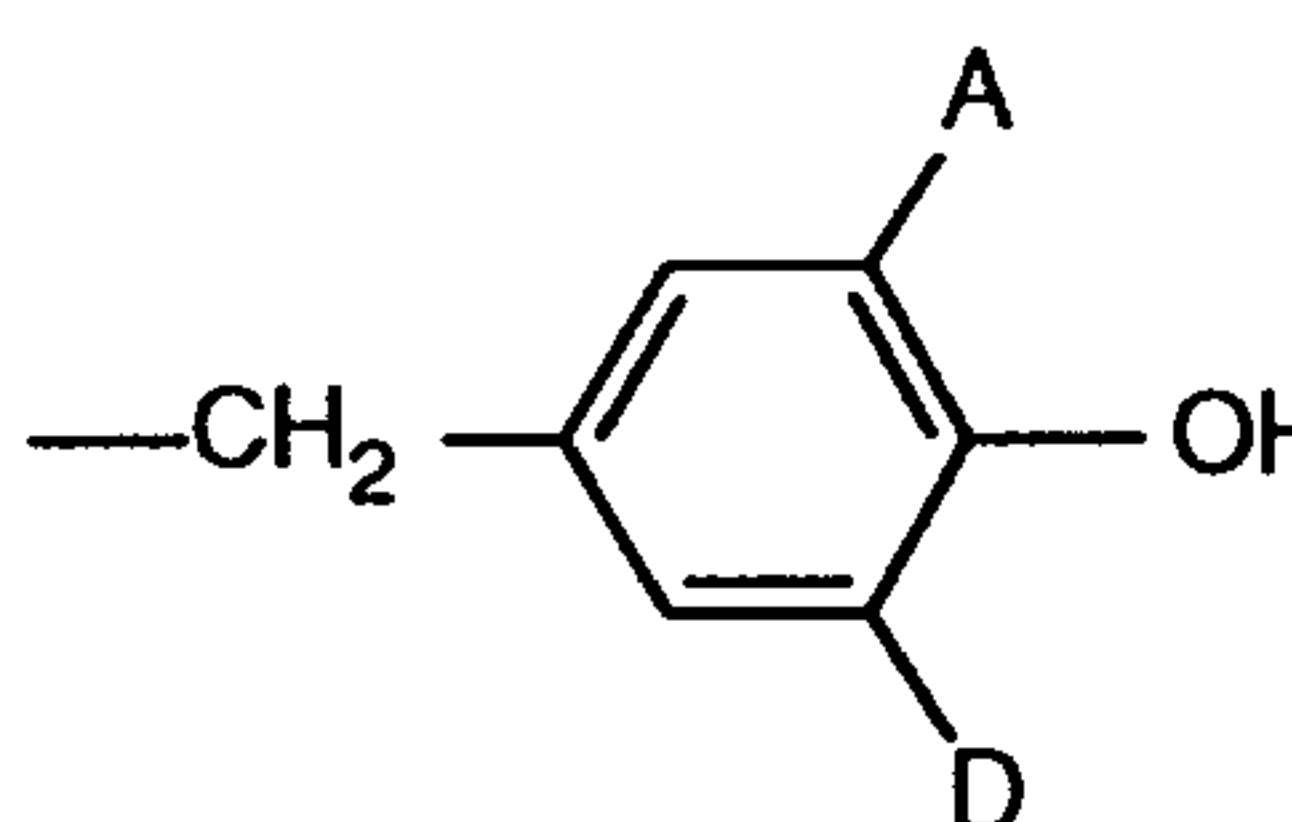


C_4 - C_8 alkylene, which may be interrupted by $-O-$ or $-NH-$, R_{18} is hydrogen,

C_1 - C_4 alkyl or phenyl, R_{19} is C_1 - C_{18} alkyl, R_{20} is hydrogen, C_1 - C_{24} alkyl, phenyl,

C_2 - C_{18} alkanoyl or benzoyl, R_{21} is C_1 - C_{18} alkyl, cyclohexyl, phenyl,



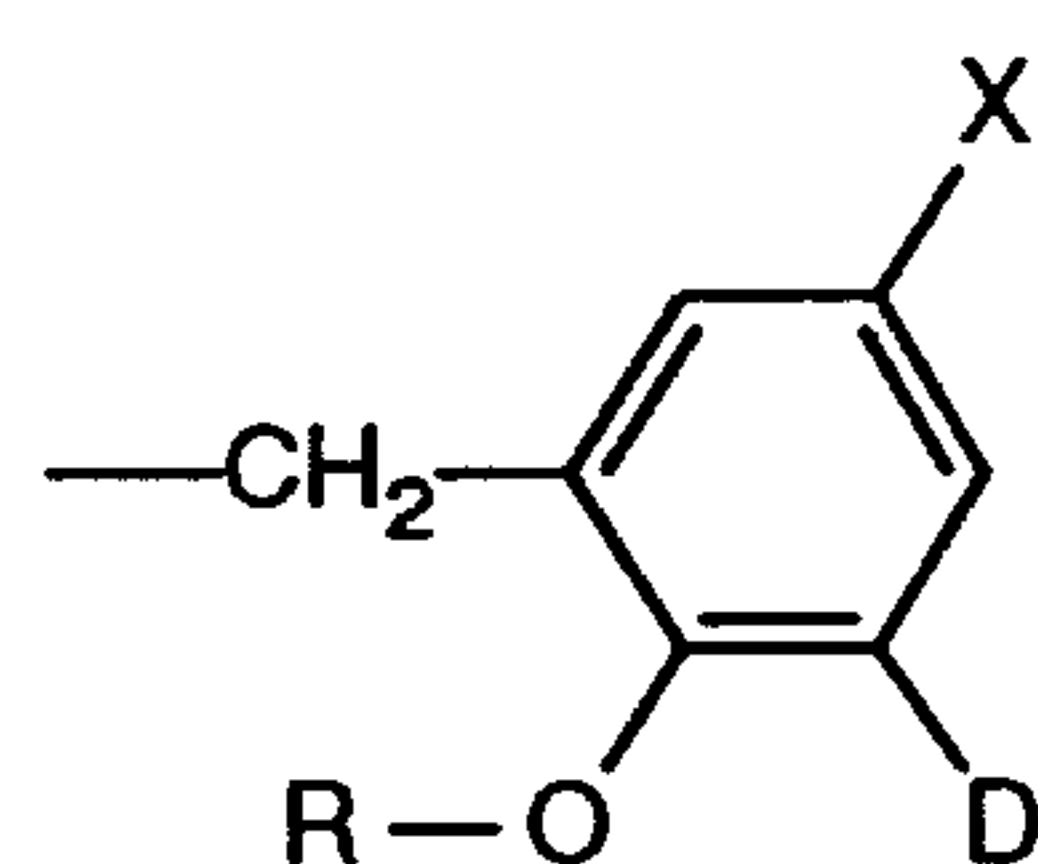
R_{22} is hydrogen, C_1 - C_{18} alkyl, cyclohexyl, or a  group, or

R_{21} and R_{22} together are C_4 - C_8 alkylene, which may be interrupted by -O- or -NH-,

R_{23} and R_{24} are -S- C_1 - C_{18} alkyl,

a 0, 1, 2 or 3, b is 0, 1, 2 or 3, c is 1 or 2, d is 1 to 5, f is 2 to 8 and q is 1, 2, 3 or 4.

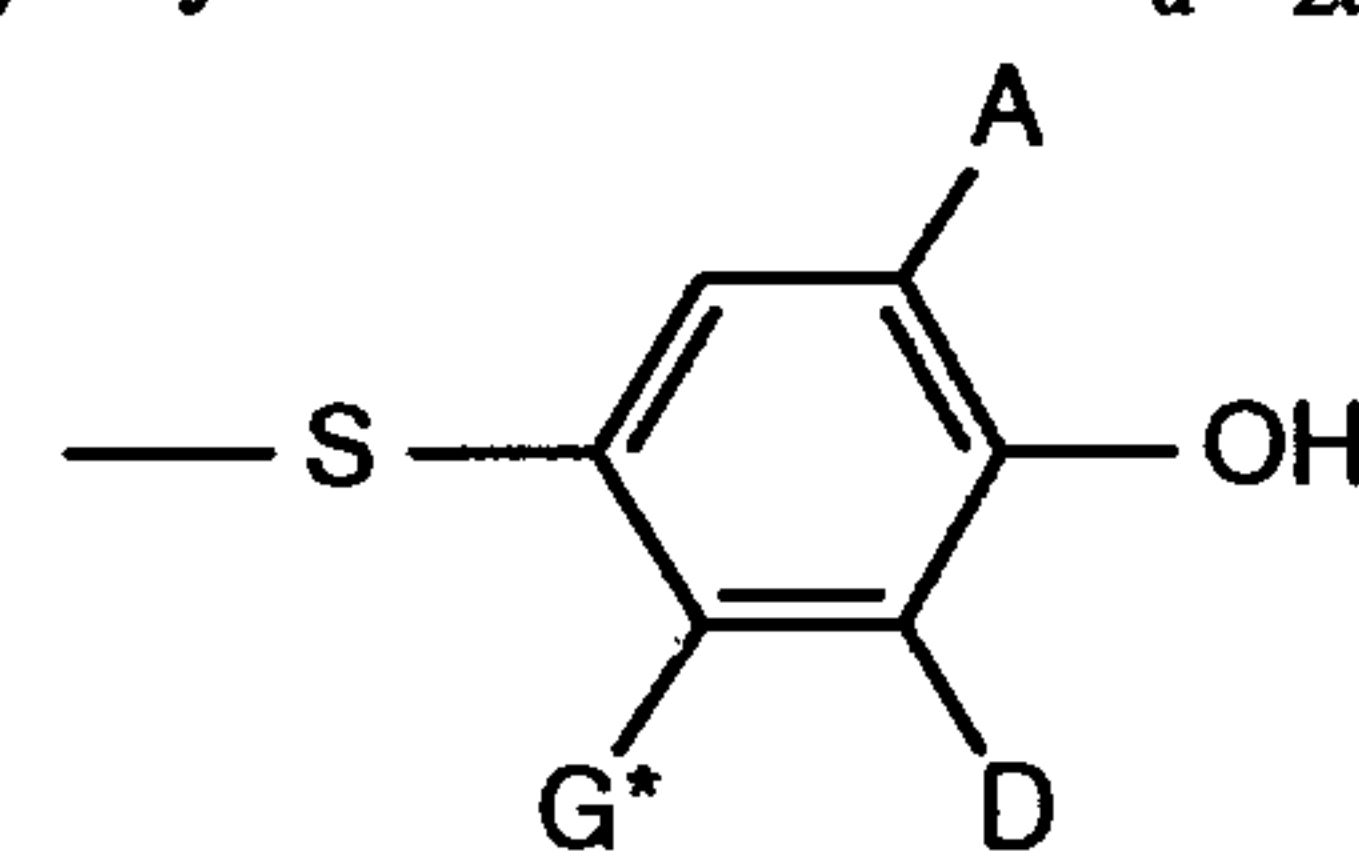
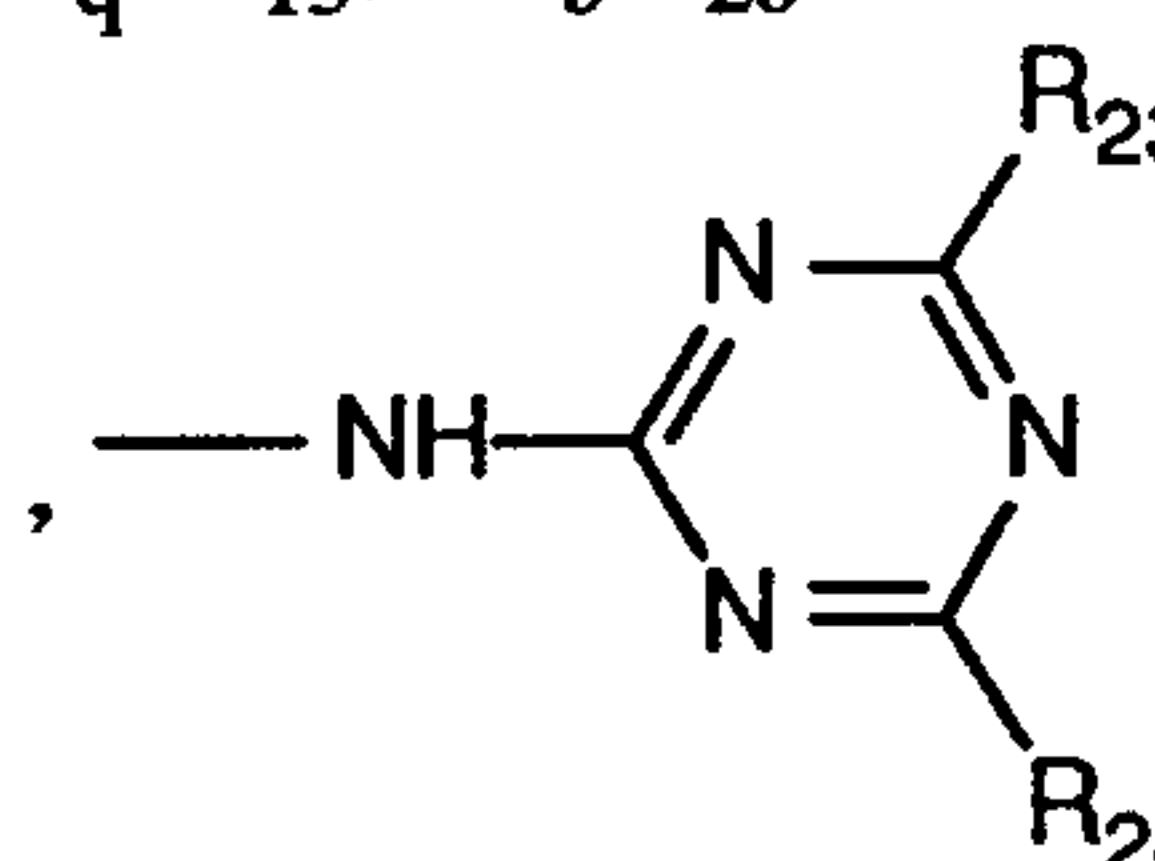
Component (c)(iii)(x) is particularly preferably a compound of the formula II' in which

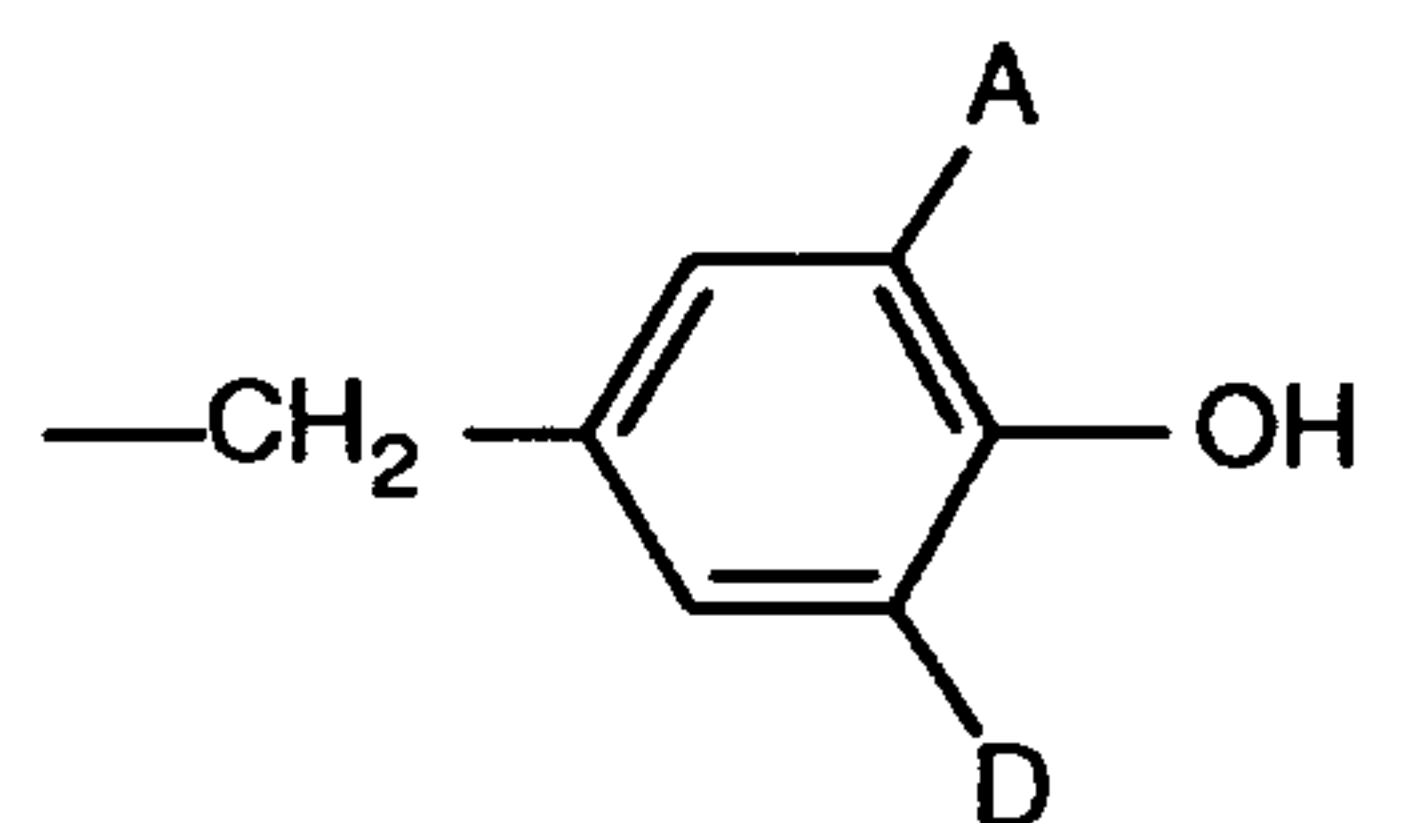
A is hydrogen, C_1 - C_8 alkyl, cyclohexyl, phenyl or a  group,

group,

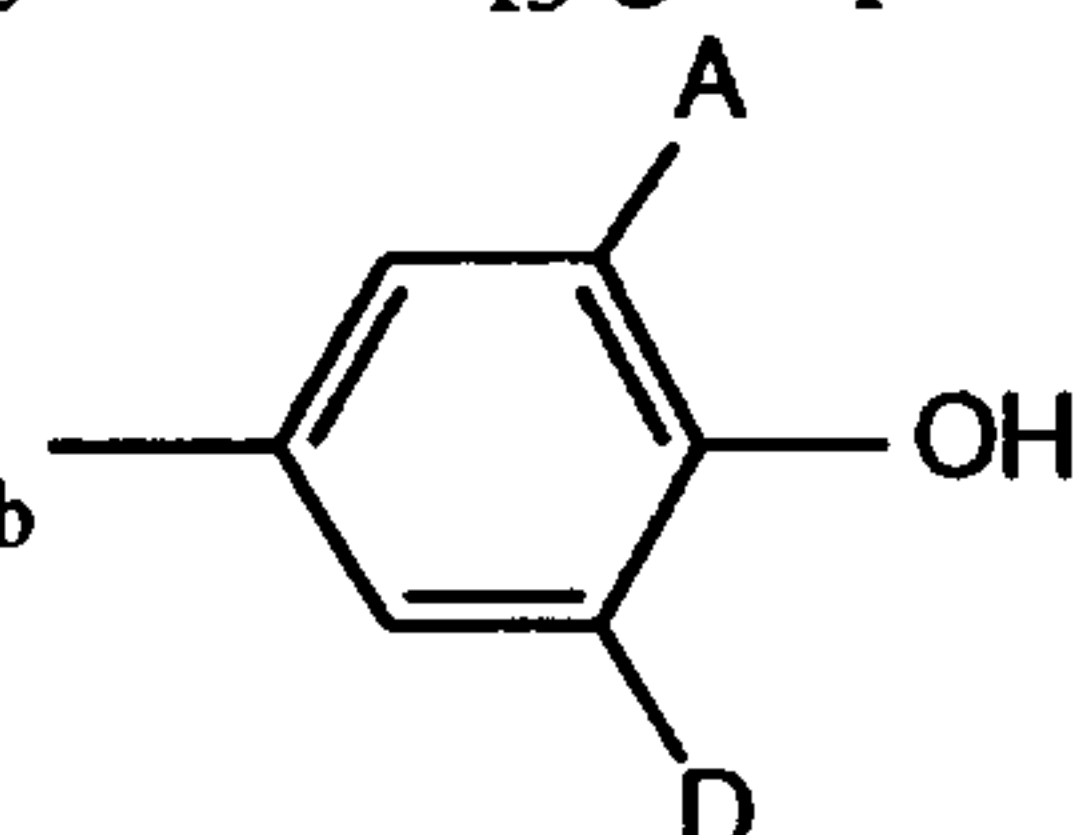
D is C_1 - C_8 alkyl, cyclohexyl, phenyl or a $-CH_2-R_{24}$ group,

X is hydrogen, C_1 - C_8 alkyl or one of the $-C_aH_{2a}-S_q-R_{13}$, $-C_bH_{2b}-CO-OR_{14}$,

$-CH_2N(R_{21})(R_{22})$, ,  or

 groups,

R_{13} is C_1 - C_{12} alkyl, phenyl or a $-(CH_2)_c-CO-OR_{15}$ group,

R_{14} is C_1 - C_{18} alkyl or a  group, in which Q is

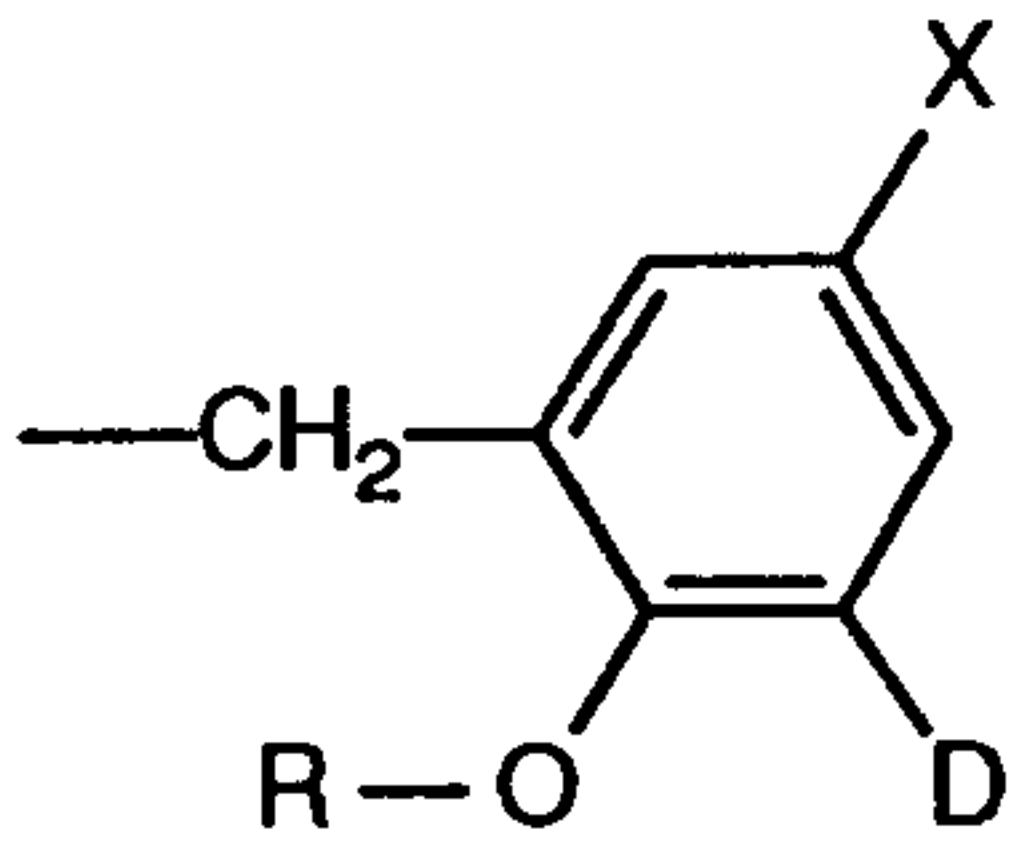
C_2 - C_8 alkylene, $-CH_2-CH_2-S-CH_2CH_2$ or a $-CH_2CH_2(OCH_2CH_2)_d-$ group,

R_{15} is C_1 - C_{18} alkyl,

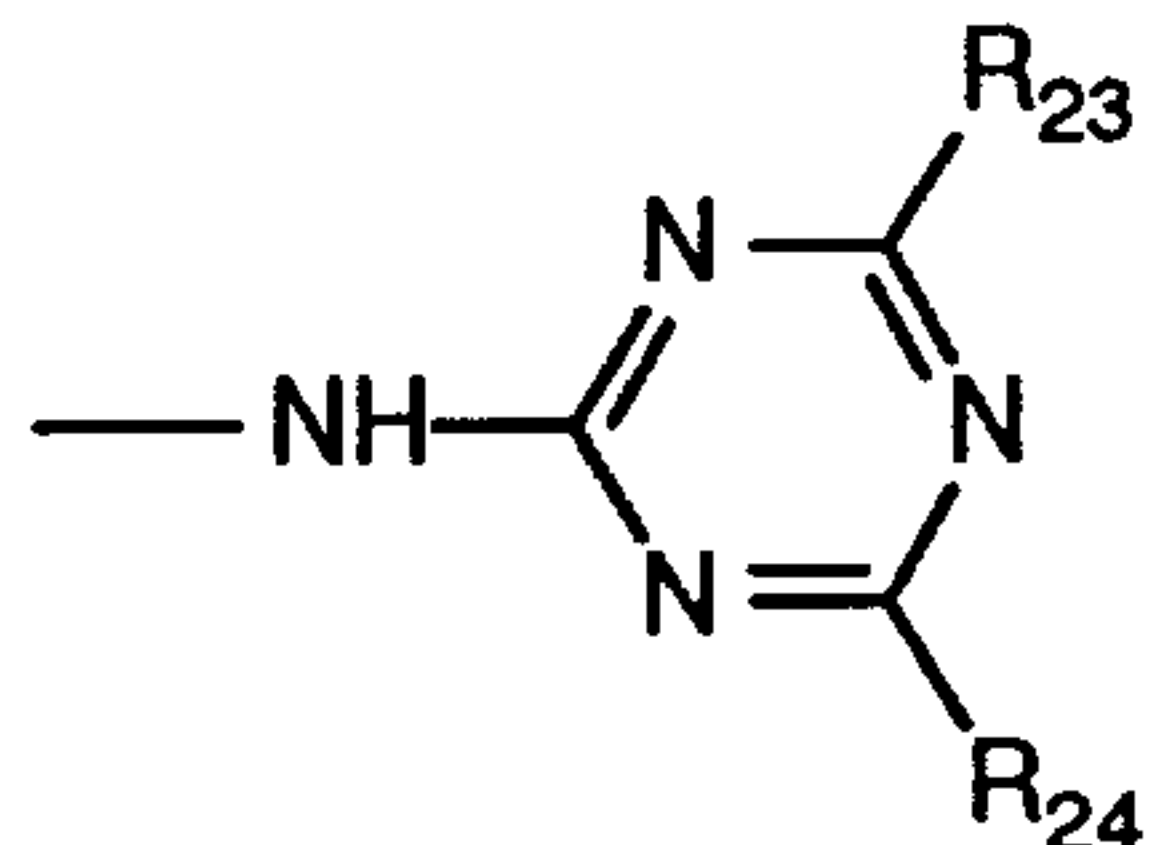
R_{21} and R_{22} , independently of one another, are hydrogen or C_1 - C_{12} alkyl or R_{21} and R_{22} together are C_4 - C_8 alkylene, which may be interrupted by -O- or -NH-,

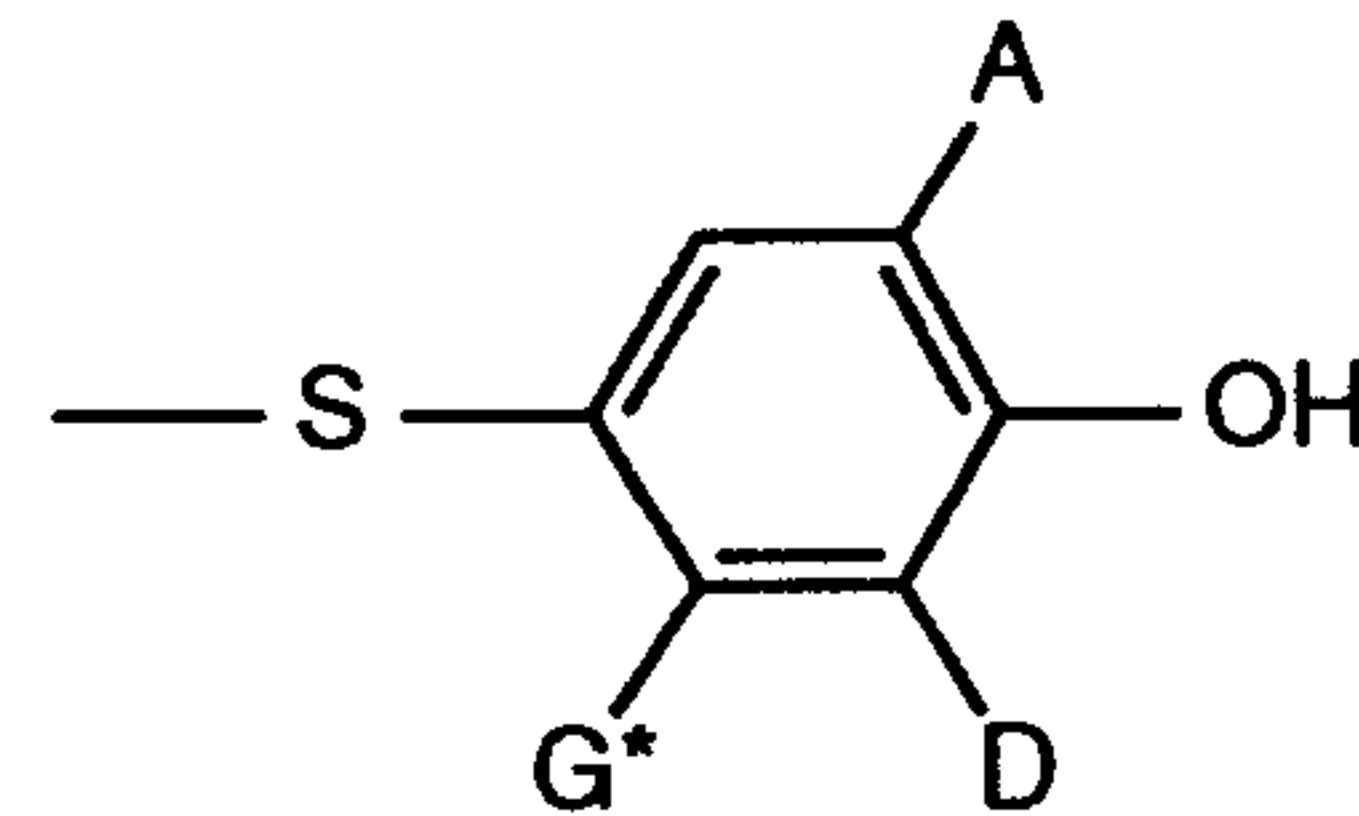
a is 1 or 2, b is 1 or 2, c is 1 or 2, and d is 1, 2 or 3, and R_{23} and R_{24} are $-S-C_1-C_{18}$ alkyl.

Component (c)(iii)(x) is very particularly a compound of the formula II' in which

A is hydrogen, C_1-C_6 alkyl, $-CH_2-R_{23}$ or a  group,

D is hydrogen or C_1-C_{18} alkyl,

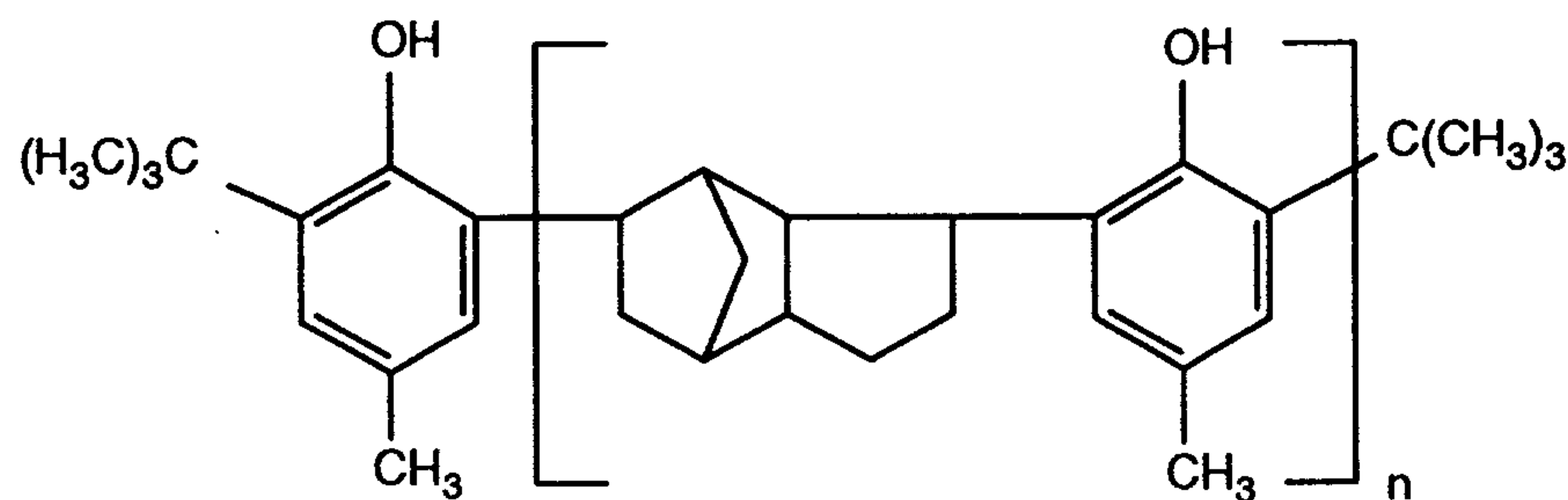
X is hydrogen, C_1-C_4 alkyl, $-CH_2-R_{23}$ or a group of the formula 

or , and

R_{23} and R_{24} are $-S-C_1-C_{18}$ alkyl.

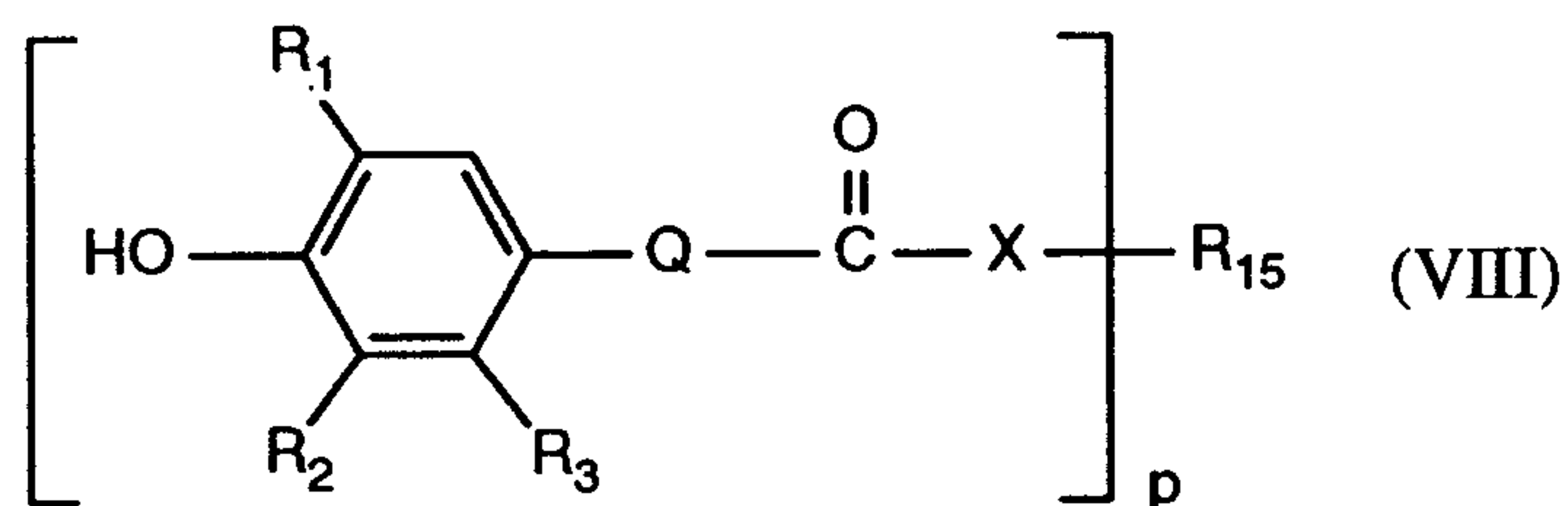
Component (c)(iii)(x) can also be a tocopherol or vitamin E derivative, for example α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol or a mixture thereof. Preference is given to vitamin E itself (α -tocopherol).

Component (c)(iii)(x) can also be an oligomeric phenolic antioxidant of the following type:



in which the mean molecular weight is from 600 to 700.

Particular preference is given to novel compositions comprising as component (c)(iii)(x) a compound of the formula VIII



in which

R_1 is C_1 - C_{18} alkyl, C_5 - C_{12} cycloalkyl, phenyl or C_7 - C_9 phenylalkyl,

R_2 is hydrogen, C_1 - C_{18} alkyl, C_5 - C_{12} cycloalkyl, phenyl or C_7 - C_9 phenylalkyl,

R_3 is hydrogen or methyl,

Q is C_mH_{2m} or $\begin{array}{c} \text{---CH}_2\text{---CH---} \\ | \\ \text{R}_{14} \end{array}$,

R_{14} is C_1 - C_8 alkyl,

X is oxygen or -NH- ,

m is the number 0, 1, 2 or 3,

p is the number 1, 2 or 4, and

if p is 1,

R_{15} is C_8 - C_{20} alkyl or C_5 - C_{12} cycloalkyl, and

if p is 2 and X is oxygen,

R_{15} is C_2 - C_8 alkylene or C_4 - C_8 alkylene which is interrupted by oxygen or sulfur; and

if p is 2 and X is -NH- ,

R_{15} is a direct bond, C_2 - C_8 alkylene or C_4 - C_8 alkylene which is interrupted by oxygen or sulfur; and

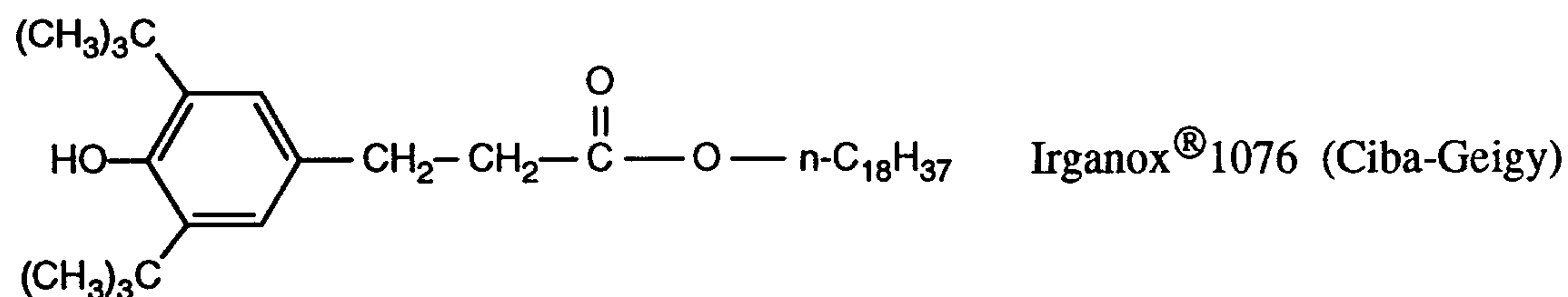
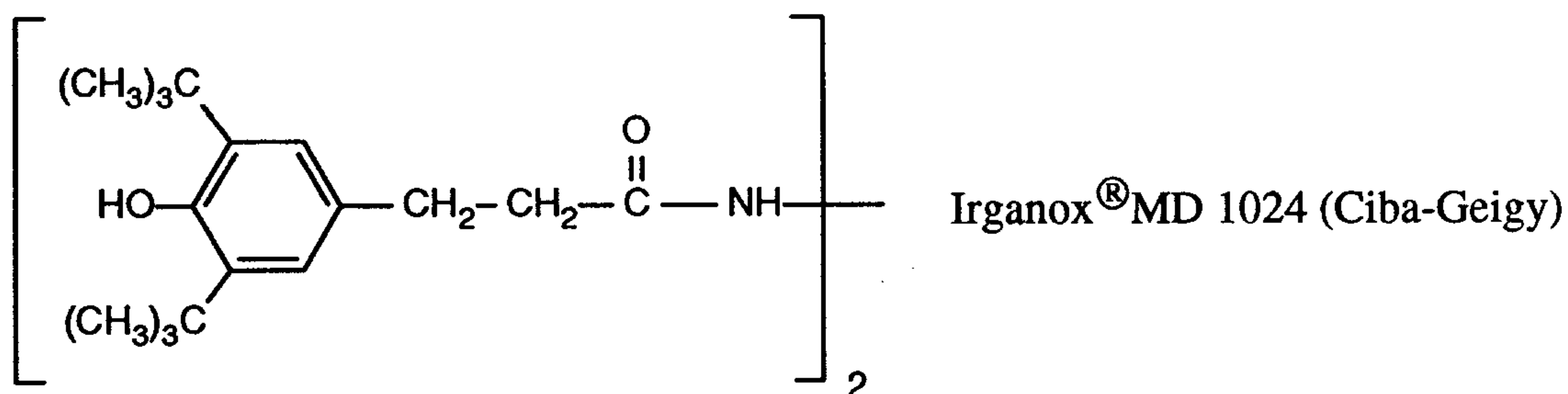
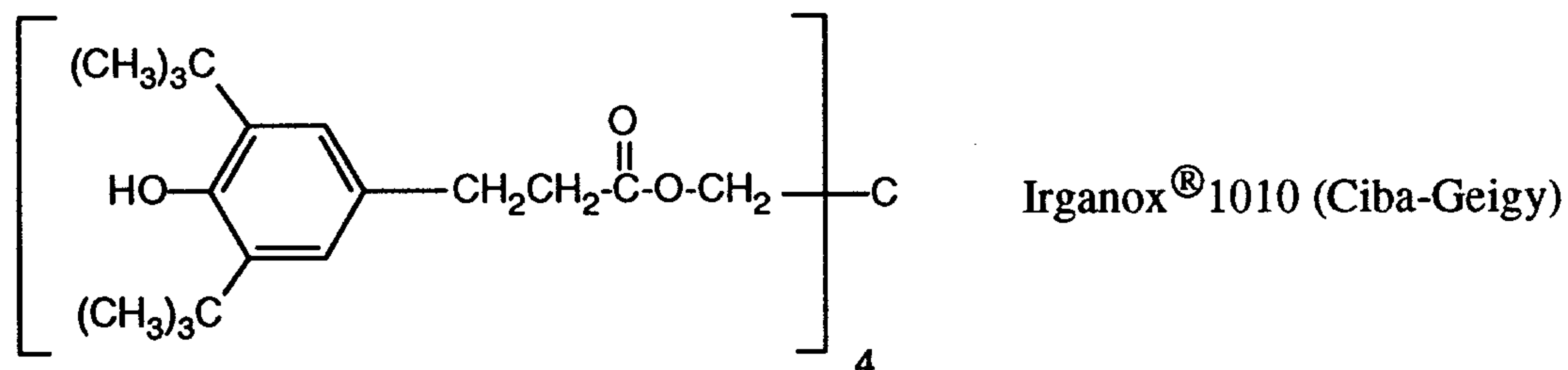
if p is 4,

R_{15} is C_4 - C_{10} alkanetetrayl.

Preferred compounds of the formula I or II as component (c)(iii)(x) in the novel compositions are the same as for component (c)(i).

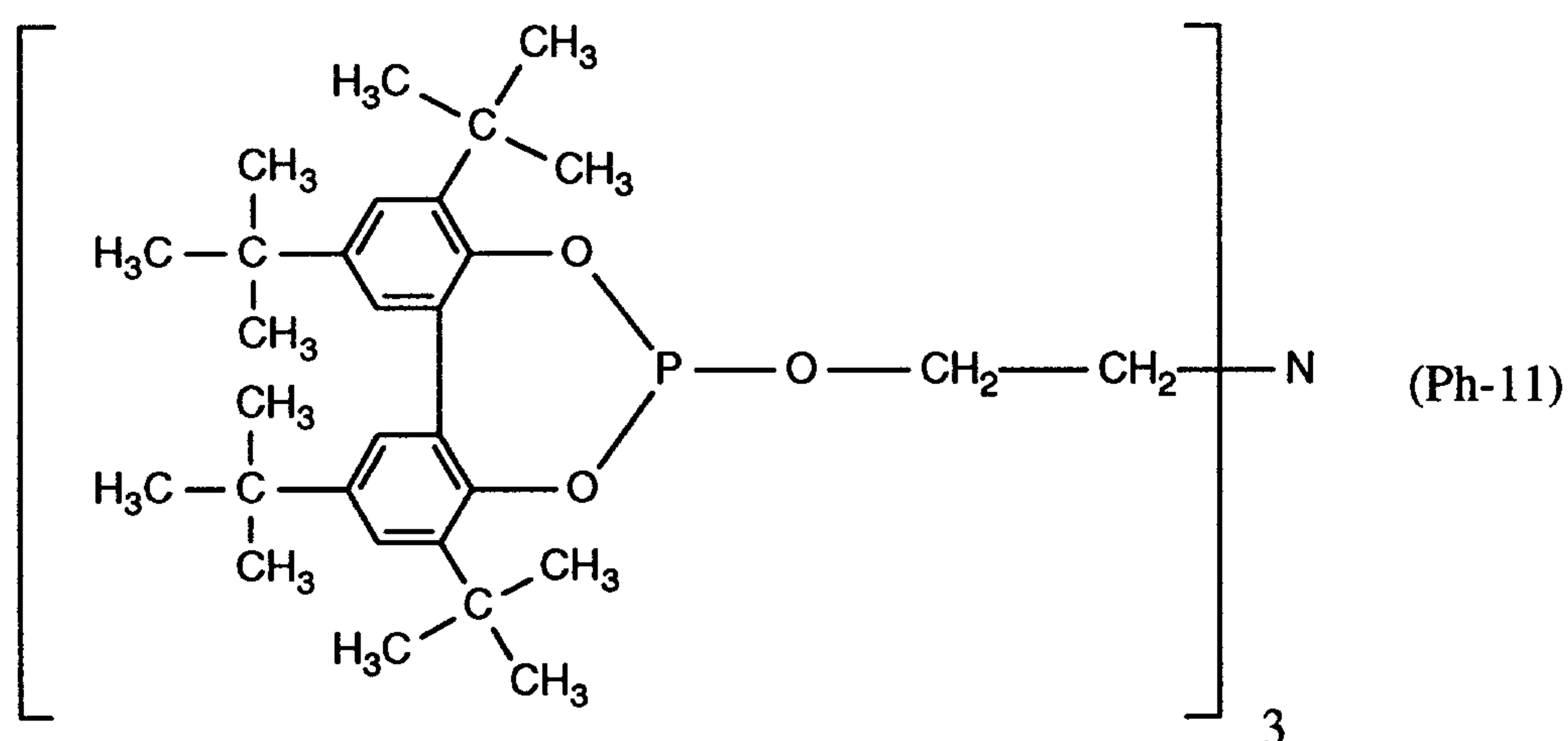
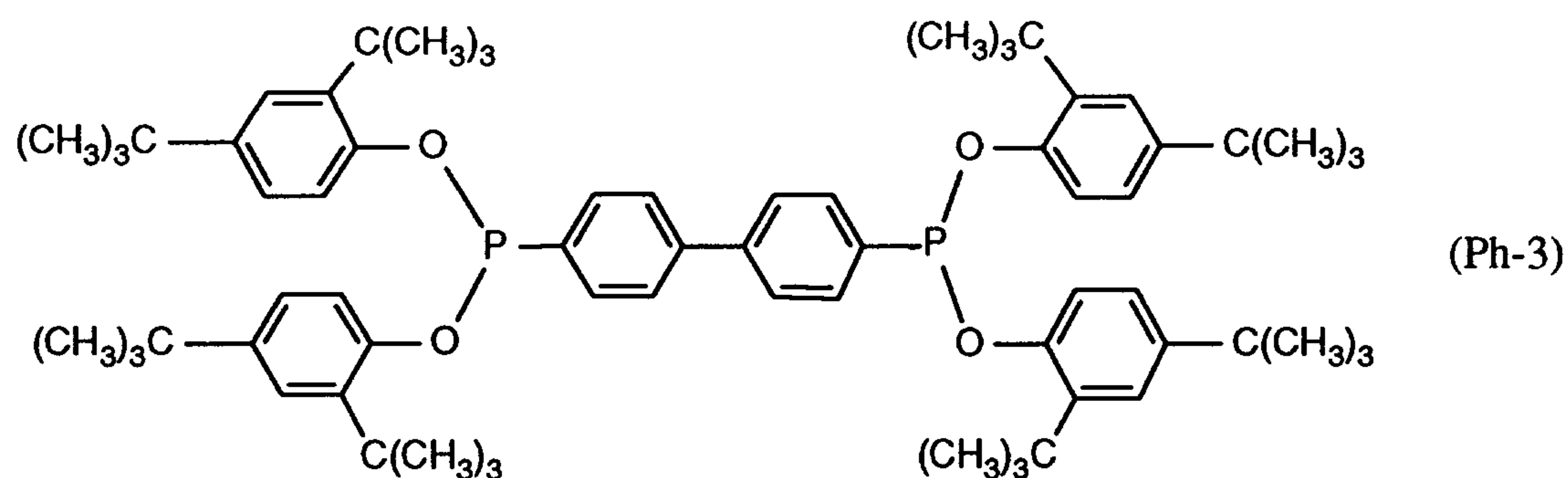
Especial preference is given to compositions comprising as component (c)(iii)(x) a compound of the formula I, II or VIII in which R_1 and R_2 are tert-butyl and m is 2.

Of very special interest are compositions comprising as component (c)(iii)(x) Irganox[®]1010 (Ciba-Geigy), Irganox[®]MD 1024 (Ciba-Geigy) and Irganox[®]1076 (Ciba-Geigy).



Preference is furthermore given to compositions comprising as component (c) a component (i) or a component (iii).

Of very special interest are compositions comprising as component (b) tris(2,4-di-tert-butylphenyl) phosphite, bis(2,4-di-tert-butyl-6-methyl) ethyl phosphite or a compound of the formula Ph-3 or Ph-11

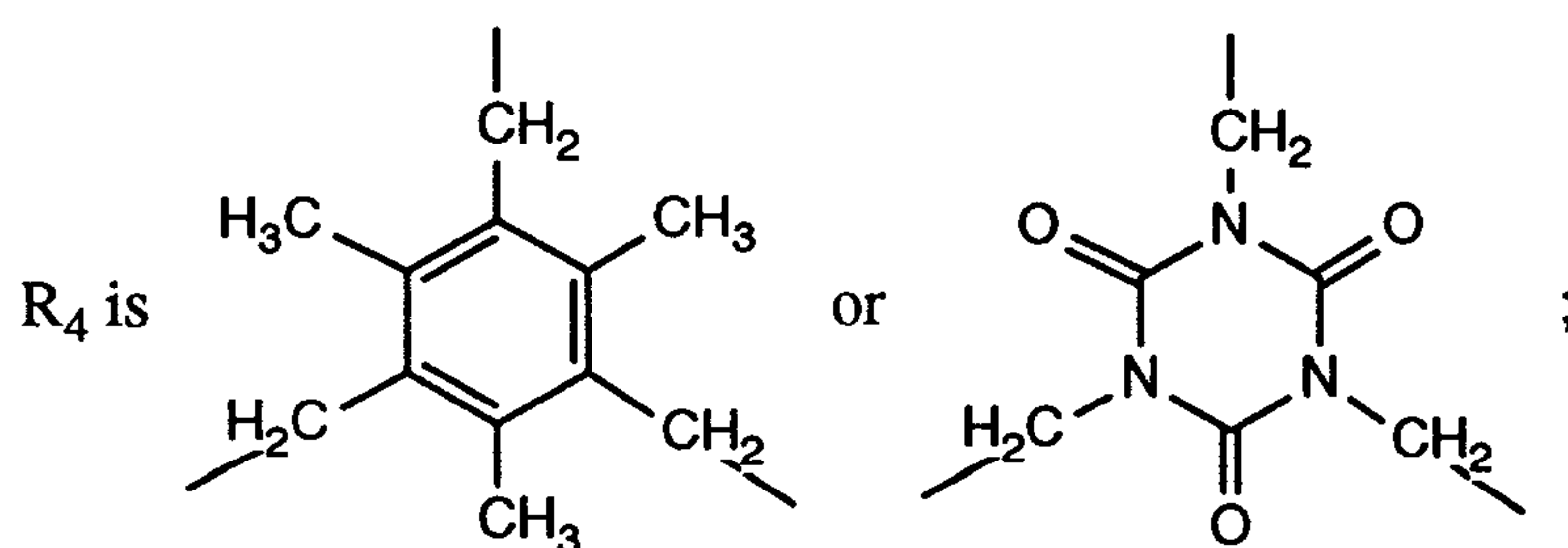


as component (c)(i) a compound of the formula I in which

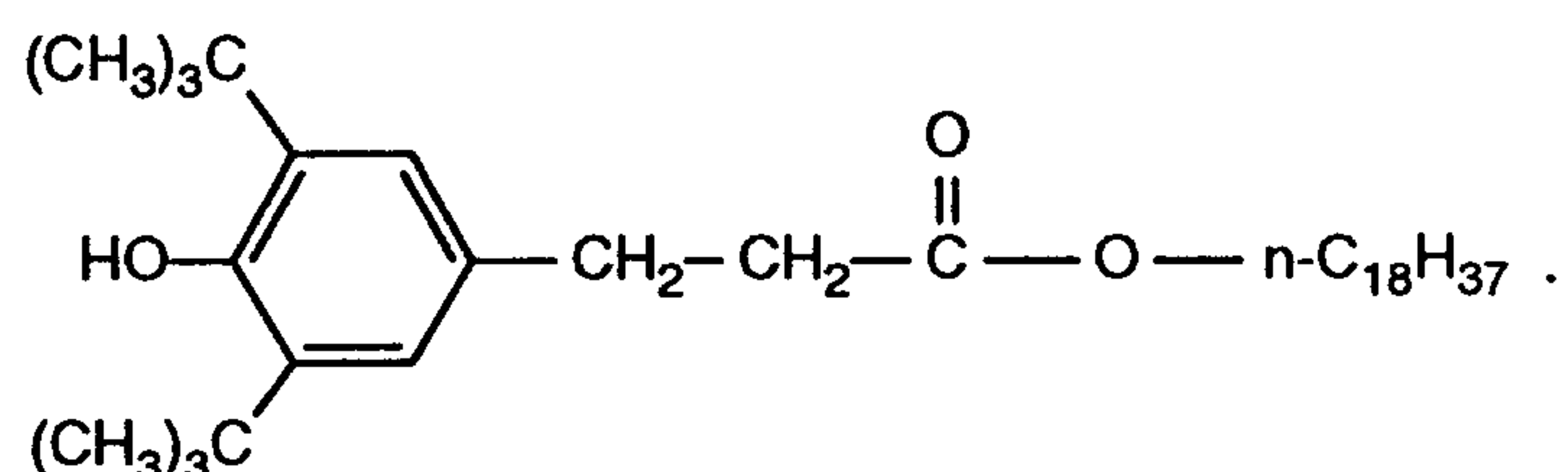
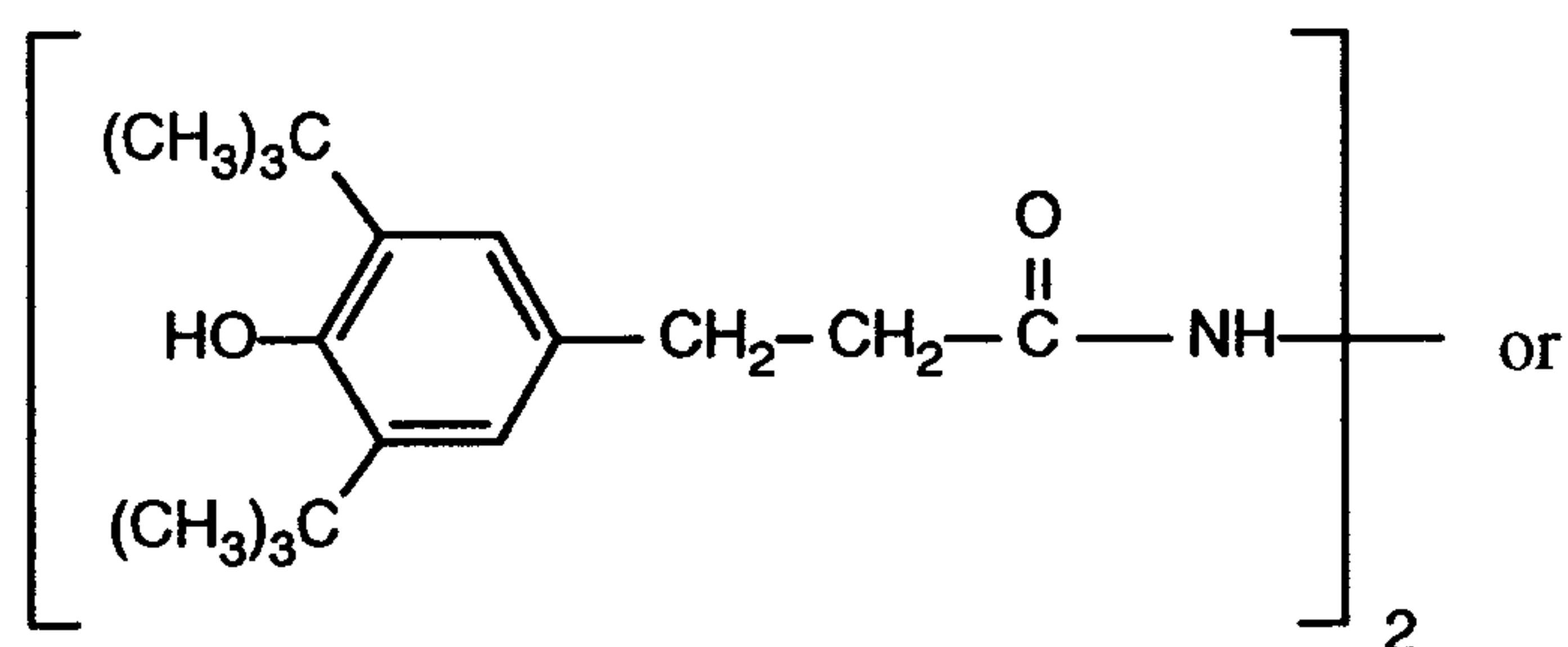
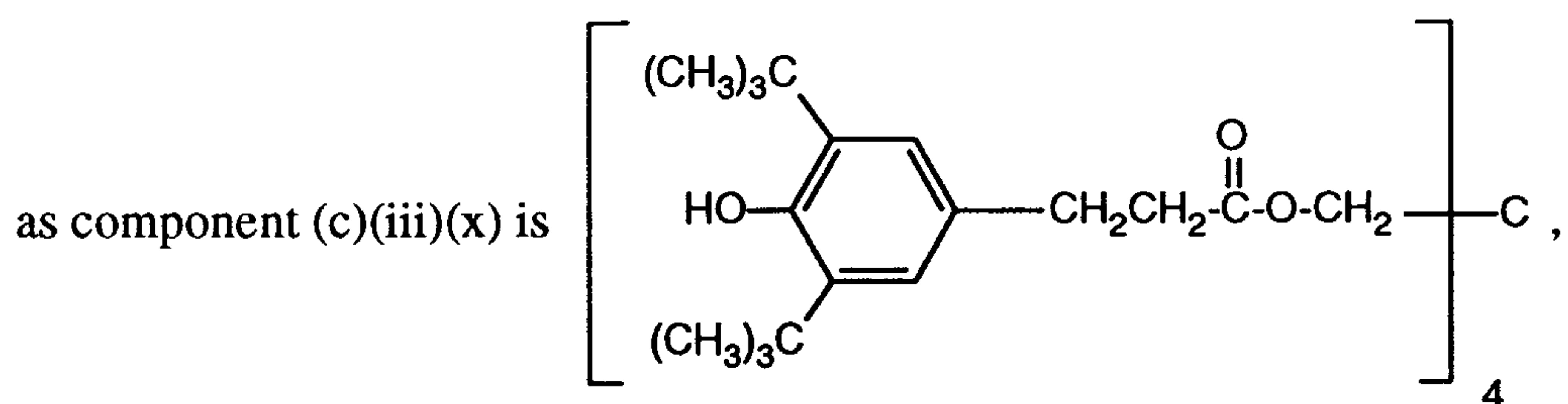
n is 3,

R_1 and R_2 are tert-butyl,

R_3 is hydrogen, and



as components (c)(ii) and (c)(iii)(y) linear or cyclic condensation products prepared from N,N' -bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine; or a condensation product prepared from 2-chloro-4,6-di(4- n -butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropyl-amino)ethane; and



Components (b) and (c) are suitable for stabilizing polyolefins which are in permanent contact with extracting media.

Examples of polyolefins are:

1. Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybut-1-ene, poly-4-methylpent-1-ene, polyisoprene or polybutadiene, as well as polymers of cycloolefins, for instance of cyclopentene or norbornene; furthermore polyethylene (which can be crosslinked, if desired), for example high density polyethylene (HDPE), high density polyethylene of high molecular weight (HDPE-HMW), high density polyethylene of ultrahigh molecular weight (HDPE-UHMW), medium density polyethylene (MDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), (VLDPE) and (ULDPE).

Polyolefins, ie. polymers of monoolefins, as mentioned by way of example in the previous paragraph, in particular polyethylene and polypropylene, can be prepared by various processes, in particular by the following methods:

- a) by means of free radicals (usually at high pressure and high temperature),
- b) by means of a catalyst, where the catalyst usually contains one or more metals from group IVb, Vb, VIb or VIII. These metals usually contain one or more ligands, such as oxides, halides, alkoxides, esters, ethers, amines, alkyls, alkenyls and/or aryls, which can be either π - or σ -coordinated. These metal complexes can be free or fixed to supports, for example to activated magnesium chloride, titanium(III) chloride, aluminum oxide or silicon oxide. These catalysts can be soluble or insoluble in the polymerization medium. The catalysts can be active as such in the polymerization or further activators can be used, for example metal alkyls, metal hydrides, metal alkyl halides, metal alkyl oxides or metal alkyl oxanes, where the metals are elements from groups Ia, IIa and/or IIIa. The activators can have been modified, for example, by means of further ester, ether, amine or silyl ether groups. These catalyst systems are usually known as Phillips, Standard Oil Indiana, Ziegler(-Natta), TNZ (DuPont), metallocene or single site catalysts (SSC).

2. Mixtures of the polymers mentioned under 1), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).

3. Copolymers of monoolefins and diolefins with each other or with other vinyl monomers, for example ethylene-propylene copolymers, linear low density polyethylene (LLDPE) and its mixtures with low density polyethylene (LDPE), propylene-but-1-ene, propylene-isobutylene, ethylene-but-1-ene, ethylene-hexene, ethylene-methylpentene, ethylene-heptene, ethylene-octene, propylene-butadiene, isobutylene-isoprene, ethylene-alkyl acrylate, ethylene-alkyl methacrylate, ethylene-vinyl acetate copolymers or copolymers thereof with carbon monoxide or ethylene-acrylic acid copolymers and their salts (ionomers) and terpolymers of ethylene with propylene and a diene, such as hexadiene, dicyclopentadiene or ethylidenenorbornene; as well as mixtures of such copolymers and their mixtures with polymers mentioned in 1), for example polypropylene-ethylene-propylene copolymers, LDPE-ethylene-vinyl acetate copolymers, LDPE-ethylene-acrylic acid copolymers, LLDPE-ethylene-vinyl acetate copolymers, LLDPE-ethylene-acrylic acid copolymers and polyalkylene-carbon monoxide copolymers with an alternating or random structure, and mixtures thereof with other polymers, for example polyamides.

4. Hydrocarbon resins (for example C₅-C₉), including hydrogenated modifications thereof (for example tackifying resins) and mixtures of polyalkylenes and starch.

Preferred polyolefins are polyethylene, polypropylene and copolymers thereof with mono-olefins and diolefins.

Particular mention should be made of the action of the stabilizer mixture comprising a component (b) and a component (c) against oxidative and thermal degradation of polyolefins, as occur during the processing of thermoplastics. The polyolefins stabilized in this way are in addition distinguished by excellent chemical resistance to extracting media with which they are in permanent contact.

Component (b) is preferably added to the polyolefin to be stabilized in an amount of from 0.02 to 0.6%, in particular from 0.05 to 0.2%, and component (c) is preferably added in an amount of from 0.02 to 1.0%, in particular from 0.05 to 0.3%, based on the weight of the polyolefin to be stabilized.

If component (c) is component mixture (c)(iii), component (c)(iii)(x) is preferably added to the polyolefin to be stabilized in an amount of from 0.02 to 0.5%, in particular from 0.05 to 0.2%, and component (c)(iii)(y) is preferably added in an amount of from 0.02 to 1.0%, in particular from 0.05 to 0.3%, based on the weight of the polyolefin to be stabilized.

In addition to components (b) and (c), the novel compositions can comprise further costabilizers (additives), for example the following:

1. Antioxidants

1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, linear or side-chain-branched nonylphenols, for example 2,6-dinonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methyl-undec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures thereof.

1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-didodecylthiomethyl-4-nonylphenol.

1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-di-phenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

1.4. Tocopherols, for example α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol and mixtures thereof (vitamin E).

1.5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl) disulfide.

1.6. Alkylidene bisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl) butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl] terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

1.7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxy-dibenzyl ether, octadecyl 4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl 4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)-amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide, isooctyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.

1.8. Hydroxybenzylated malonates, for example dioctadecyl 2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl)malonate, dioctadecyl 2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)malonate, didodecylmercaptoethyl 2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, di[4-(1,1,3,3-tetramethylbutyl)phenyl] 2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

1.9. Hydroxybenzyl aromatic compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

1.10. Triazine compounds, for example 2,4-bis(octylmercapto-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenyl-propionyl)hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)-isocyanurate.

1.11. Benzylphosphonates, for example dimethyl 2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, calcium salt of monoethyl 3,5-di-tert-butyl-4-hydroxybenzyl phosphonate.

1.12. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.

1.13. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with monohydric or polyhydric alcohols, for example with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol,

thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-[2.2.2]octane.

1.14. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with monohydric or polyhydric alcohols, for example methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-[2.2.2]octane.

1.15. Esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with monohydric or polyhydric alcohols, for example methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-[2.2.2]octane.

1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenylacetic acid with monohydric or polyhydric alcohols, for example methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-[2.2.2]octane.

1.17. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, for example N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine, N,N'-bis[2-(3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyloxy)ethyl]oxalamide.

1.18. Ascorbic acid (vitamin C).

1.19. Aminic antioxidants, for example N,N'-di-isopropyl-p-phenylenediamine, N,N'-di-

sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-di-(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfonamido)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, di-(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-di[(2-methylphenyl)amino]ethane, 1,2-di(phenylamino)propane, (o-tolyl)biguanide, di[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, mixture of mono- and dialkylated nonyldiphenylamines, mixture of mono- and dialkylated dodecyldiphenylamines, mixture of mono- and dialkylated isopropyl/isohexyldiphenylamines, mixture of mono- and dialkylated tert-butyldiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, mixture of mono- and dialkylated tert-butyl/tert-octylphenothiazines, mixture of mono- and dialkylated tert-octylphenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine, bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol.

2. UV absorbers and light stabilizers

2.1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octoxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis(α,α -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, mixture of 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonyl)ethyl)-

phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonyl-ethyl]-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl-ethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl-ethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonyl-ethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonyl-ethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, and 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonyl-ethyl)phenyl)benzotriazole, 2,2'-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazol-2-yl phenol]; transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonyl-ethyl)-2'-hydroxyphenyl]benzotriazole with polyethylene glycol 300; $[R-CH_2CH_2-COO(CH_2)_3]_n$ where R = 3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-yl phenyl.

2.2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octoxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

2.3. Esters of unsubstituted or substituted benzoic acids, for example 4-tert-butyl-phenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis(4-tert-butylbenzoyl)resorcinol, benzoylresorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2.4. Acrylates, for example ethyl and isooctyl α -cyano- β,β -diphenylacrylate, methyl α -carbomethoxycinnamate, methyl and butyl α -cyano- β -methyl-p-methoxycinnamate, methyl α -carbomethoxy-p-methoxycinnamate and N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

2.5. Nickel compounds, for example nickel complexes of 2,2'-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol], such as the 1:1 and 1:2 complexes, if desired with additional ligands, such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of monoalkyl esters, such as the methyl or ethyl esters, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of ketoximes, such as of 2-hydroxy-4-methylphenyl undecyl ketoxime, and nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, if desired with additional ligands.

2.6. Sterically hindered amines, for example bis(2,2,6,6-tetramethylpiperidin-4-yl) seba-

cate, bis(2,2,6,6-tetramethylpiperidin-4-yl) succinate, bis(1,2,2,6,6-pentamethylpiperidin-4-yl) sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate, bis(1,2,2,6,6-pentamethylpiperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the product of the condensation of 1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, the product of the condensation of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-s-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl) nitrilotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl) 1,2,3,4-butanetetraoate, 1,1'-(1,2-ethanediyl)bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl) malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl) sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl) succinate, the product of the condensation of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the product of the condensation of 2-chloro-4,6-di-(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the product of the condensation of 2-chloro-4,6-di(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearyloxy-2,2,6,6-tetramethylpiperidine, the product of the condensation of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, the product of the condensation of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine, and also 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136504-96-6]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxospiro[4,5]decane, and the product of the reaction of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro [4,5]decane and epichlorohydrin.

2.7. Oxalamides, for example 4,4'-dioctyloxyoxanilide, 2,2' diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butyloxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butyloxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxalamide, 2-ethoxy-5-tert-butyl-2'-ethyloxanilide and mixtures thereof with 2-ethoxy-2'-ethyl-5,4'-di-tert-butyl-oxanilide, and mixtures of o- and p-methoxy- and of o- and p-ethoxy-disubstituted oxanilides.

2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propoxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butoxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxypropoxy)phenyl]-1,3,5-triazine, 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine.

3. Metal deactivators, for example N,N'-diphenyloxalamide, N-salicylal-N'-salicyloylhydrazine, N,N'-bis(salicyloyl)hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalodihydrazide, oxanilide, isophthalodihydrazide, sebacobisphenyl hydrazide, N,N'-diacetyladihydrazide, N,N'-bissalicyloyloxalodihydrazide and N,N'-bissalicyloylthiopropionodihydrazide.

4. Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythrityl diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythrityl diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythrityl diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythrityl diphosphite, bis-isodecyloxy pentaerythrityl diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) pentaerythrityl diphosphite, bis(2,4,6-tri-tert-butylphenyl) pentaerythrityl diphosphite, tristearyl sorbityltriposphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylenediphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocine, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyldibenz[d,g]-1,3,2-dioxaphosphocine, bis(2,4-di-tert-butyl-6-methylphenyl) methyl phosphite and bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite.

5. Hydroxylamines, for example N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine made from hydrogenated tallow fatty amines.

6. Nitrones, for example N-benzyl-alpha-phenyl nitrone, N-ethyl-alpha-methyl nitrone, N-octyl-alpha-heptyl nitrone, N-lauryl-alpha-undecyl nitrone, N-tetradecyl-alpha-tridecyl nitrone, N-hexadecyl-alpha-pentadecyl nitrone, N-octadecyl-alpha-heptadecyl nitrone, N-hexadecyl-alpha-heptadecyl nitrone, N-octadecyl-alpha-pentadecyl nitrone, N-heptadecyl-alpha-heptadecyl nitrone, N-octadecyl-alpha-hexadecyl nitrone, nitrones derived from N,N-dialkylhydroxylamines prepared from hydrogenated tallow fatty amines.

7. Thiosynergists, for example dilauryl thiodipropionate and distearyl thiodipropionate.

8. Peroxide scavengers, for example esters of β -thiodipropionic acid, for example the lauryl, stearyl, myristyl and tridecyl esters, mercaptobenzimidazole, the zinc salt of 2-mercaptobenzimidazole, zinc dibutyldithiocarbamate, dioctadecyl disulfide and pentaerythrityl tetrakis(β -dodecylmercapto)propionate.

9. Polyamide stabilizers, for example copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

10. Basic costabilizers, for example melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali and alkaline earth metal salts of higher fatty acids, for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate, potassium palmitate, antimony pyrocatecholate and tin pyrocatecholate.

11. Nucleating agents, for example inorganic substances, for example talc, metal oxides, such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates, preferably of alkaline earth metals; organic compounds, such as mono- or polycarboxylic acids, and salts thereof, for example 4-tert-butylbenzoic acid, adipic acid and diphenylacetic acid, sodium succinate or sodium benzoate; polymeric compounds, for example ionic copolymers ("ionomers").

12. Fillers and reinforcing agents, for example calcium carbonate, silicates, glass fibres, glass beads, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, sawdust and flours or fibres of other natural products, synthetic fibres.

13 Other additives, for example plasticizers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow aids, optical brighteners, flameproofing agents, antistatic and blowing agents.

14. Benzofuranones and indolinones, as described, for example, in US-A-4 325 863, US-A-4 338 244, US-A-5 175 312, US-A-5 216 052, US-A-5 252 643, DE-A-4 316 611, DE-A-4 316 622, DE-A-4 316 876, EP-A-0 589 839 or EP-A-0 591 102, or 3-[4-(2-acetoxyethoxy)phenyl]-5,7-di-tert-butyl-benzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)benzofuran-2-one], 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one, 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one and 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butylbenzofuran-2-one.

With the exception of the fillers and reinforcing agents (point 12 in the list), the costabilizers are added to the polyolefin in, for example, concentrations of from 0.01 to 10%, based on the total weight of the polyolefin to be stabilized.

The fillers and reinforcing agents (point 12 in the list) such as, for example, talc, calcium carbonate, mica or kaolin are added to the polyolefin in, for example, concentrations of from 0.01 to 40%, based on the total weight of the polyolefin to be stabilized.

Fillers and reinforcing agents (point 12 in the list) such as, for example, metal hydroxides, in particular aluminium hydroxide or magnesium hydroxide, are added to the polyolefin in, for example, concentrations of from 0.01 to 60%, based on the total weight of the polyolefin to be stabilized.

Carbon black as filler is expediently added to the polyolefin in concentrations of from 0.01 to 5%, based on the total weight of the polyolefin to be stabilized.

Glass fibres as reinforcing agents are expediently added to the polyolefin in concentrations

of from 0.01 to 20%, based on the total weight of the polyolefin to be stabilized.

In addition to components (a), (b) and (c), further preferred compositions also comprise further additives, in particular UV absorbers and light stabilizers (point 2 in the list); amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid (metal deactivators, point 1.17 in the list); nucleating agents (point 11 in the list) and/or fillers and reinforcing agents (point 12 in the list).

Of particular interest as additional additives are metal deactivators, for example N,N'-bis-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine [Irganox[®]MD1024 (Ciba-Geigy)] or N,N'-bis[2-(3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyloxy)ethyl]oxamide [Naugard[®]XL-1 (Uniroyal)].

Components (b) and (c) and any further additives used are incorporated into the polyolefin by known methods, for example before or during shaping or alternatively by applying the dissolved or dispersed stabilizer mixture to the polyolefin, if necessary with subsequent evaporation of the solvent. The stabilizer mixture of components (b) and (c) can also be added to the polyolefins to be stabilized in the form of a masterbatch in which these components are present, in a concentration of from 2.5 to 25% by weight.

The stabilizer mixtures comprising components (b) and (c) can also be added before or during the polymerization or before the crosslinking.

The stabilizer mixtures comprising components (b) and (c) can be incorporated into the polyolefin to be stabilized in pure form or encapsulated in waxes, oils or polymers.

Components (b) and (c), or mixtures thereof, can also be sprayed onto the polyolefin to be stabilized. They are capable of diluting other additives (for example the abovementioned conventional additives) or melts thereof, so that they can also be sprayed onto the polyolefin to be stabilized together with these additives. A particularly advantageous procedure is addition before spraying, during deactivation of the polymerization catalysts, in which case for example, the steam for deactivation can be used for the spraying.

In the case of polyolefins polymerized in spherical form, it may be advantageous, for example, to apply components (b) and (c), if desired together with other additives, by spraying.

The polyolefins stabilized in this way can be used in a wide variety of forms, in particular as thick-walled polyolefin mouldings, which are in permanent contact with extracting media, for example pipes for liquids or gases, sheeting, geomembranes, tapes, profiles or tanks.

The present invention also relates to a process for stabilizing thick-walled polyolefin mouldings which are in permanent contact with extracting media, which comprises incorporating or applying a mixture comprising a component (b) and a component (c) to these mouldings.

Preference is given to a process for stabilizing thick-walled polyolefin mouldings which are in permanent contact with extracting media in which the thick-walled polyolefin mouldings have a wall thickness of from 1 to 50 mm, in particular from 1 to 30 mm, for example from 2 to 10 mm.

Also of particular interest is a process for stabilizing thick-walled polyolefin mouldings which are in permanent contact with extracting media, in which the thick-walled polyolefin mouldings are pipes or geomembranes.

The term geomembrane is taken to mean sheeting which is used, for example, in landfill sites and must have, for example, a life of up to 300 years.

Extracting media are, for example, liquid or gaseous inorganic or organic materials.

Examples of gaseous inorganic materials are oxygen; nitrogen; nitrogen oxides, for example NO, laughing gas or NO₂; sulfur oxides, for example sulfur dioxide; halogens, for example fluorine or chlorine; Brönsted acids, for example hydrofluoric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid or hydrocyanic acid, or bases, for example ammonia.

Examples of gaseous organic materials are C₁-C₄alkanes, for example methane, ethane, propane or butane; carbon monoxide; carbon dioxide; or phosgene.

Examples of liquid inorganic materials are water, chlorinated drinking water or aqueous saline solutions, for example sodium chloride solution (brine) or sodium sulfate solution;

bromine; acid halides, for example titanium tetrachloride, thionyl chloride, nitrosyl chloride or trimethylsilyl chloride; caustic lyes, for example aqueous sodium hydroxide (NaOH) solution, aqueous potassium hydroxide (KOH) solution, aqueous ammonia solution, aqueous sodium bicarbonate solution or aqueous soda solution.

Examples of liquid organic materials are organic solvents and liquid organic reagents.

Examples of organic solvents are aliphatic hydrocarbons, for example pentane, hexane, heptane, octane, gasoline, nonane or decane; alcohols, for example methanol, ethanol, isopropanol, butanol, pentanol, amyl alcohol, cyclohexanol, pentaerythritol, ethylene glycol, ethylene diglycol, methylcellosolve, polyethylene glycol or glycerol; ketones, for example acetone, diethyl ketone, methyl ethyl ketone, diphenyl ether or cyclohexanone; ethers, for example diethyl ether, dibutyl ether, tetrahydrofuran or dioxane; aromatic hydrocarbons, for example benzene, toluene or xylene; heterocyclic solvents, for example furan, pyridine, 2,6-lutidine or thiophene; dipolar aprotic solvents, for example dimethylformamide, diethylacetamide or acetonitrile; or surfactants.

Other extracting media according to the present invention are mixtures and solutions, in particular aqueous mixtures, emulsions or solutions, of liquid or gaseous inorganic and organic materials as listed above.

Of particular interest are extracting media which are of importance in the chemical industry or in landfill sites.

A preferred embodiment of the present invention is therefore the use of a mixture comprising a component (b) and a component (c) for stabilizing thick-walled polyolefin mouldings which are in permanent contact with extracting media.

The examples below illustrate the invention in greater detail. The parts and percentages are by weight.

Example 1: Stability of polyethylene which is in permanent contact with water and which has been stabilized by means of a component (b) and a component (c)(i).

The unstabilized medium-density polyethylene (PE-MD) used has the material properties summarized in Table 1.

Table 1: Material properties of the polyethylene at 23°C

Property	Value	Unit	Test method
Density	0.934	g/cm ³	ISO 1872
MFI 190/2.16 MFI 190/5.00	0.15 0.55	g/10 min g/10 min	ISO 1133
Yield stress σ_s	18	N/mm ²	ISO 6259
Elongation ϵ_s	9	%	ISO 6259
Elongation at break ϵ_r	>600	%	ISO 6259
Tangential modulus	550	N/mm ²	ISO 6259
Hardness	58	Shore D	ISO 868
Vicat softening point	118	°C	ISO 306 A-50
Crystalline melting point	123-127	°C	DSC

0.1 % by weight of calcium stearate and the stabilizers listed in Table 2 are added in dry form to the polyethylene polymer removed directly from the reactor, and are incorporated for 2 minutes in a Pappenmaier mixer (type 20) (Examples 1a, 1b and 1c).

Table 2:

Example	Stabilizer	Amount (% by weight)	Molar mass (g/mol)	m.p. (°C)
Example 1a	Irgafos 168 ^{a)}	0.1	647	180-185
	Irganox 1010 ^{b)}	0.1	1178	110-125
Example 1b	Irgafos 168 ^{a)}	0.1	647	180-185
	Irganox 1330 ^{c)}	0.1	775	241-245
Example 1c	Irgafos 168 ^{a)}	0.1	647	180-185
	Irganox 3114 ^{d)}	0.1	784	218-223

- a) Irgafos[®] 168 (Ciba-Geigy) is tris(2,4-di-tert-butylphenyl) phosphite (formula Ph-2).
- b) Irganox[®] 1010 (Ciba-Geigy) is the pentaerythrityl ester of 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid.
- c) Irganox[®] 1330 (Ciba-Geigy) is 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene.
- d) Irganox[®] 3114 (Ciba-Geigy) is 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate.

In an extruder from Dolci, Milan (screw geometry $(L/D) = 35$, screw speed 55 revolutions/minute, maximum die temperature 190°C, cooling of the feed zone), the stabilized polyolefin is homogenized and converted into about 60 kg of granules per formulation. For the extraction experiments in water, test sheets measuring 200 mm x 150 mm x 2 mm are pressed out of the granules of the individual formulations (Examples 1a, 1b and 1c) using the machine parameters laid down in Table 3

Table 3: Machine parameters for test sheets

Melting time (min)	4
Pressing temperature (°C)	180
Pressing force (kN)	100
Pressing time (min)	4
Cooling time (min)	5
Cooling medium	water

by means of a bench press. In order to simplify demoulding of the test sheets, the pressing operation is carried out between two aluminium foils.

The stabilizer extraction experiments are carried out using deionized water. The extraction container is conditioned in a fan-assisted oven from Heraeus (Hanau, Germany) at a maximum temperature deviation of 1.5°C. For the extraction experiments below the boiling point of water, glass vessels are used. At a water temperature of 105°C, pressurized containers of stainless steel are used. Owing to the risk of oversaturation of the water with stabilizer, the amount of liquid for the experiments is set at about 400 ml for about 70 g of

polymer, and the water is replaced by fresh water at regular intervals, i.e. after each sample is taken.

The test sheets are exposed to the above-described experimental conditions for up to 16,032 hours (668 days). When the extraction experiments are complete, the oxidation temperature (T_{ox}) of the test sheets is determined. The determination of the oxidation temperature is carried out by means of a DuPont 910 differential scanning calorimeter from TA Instruments (Alzenau, Germany) and using from 5 to 10 mg of sample and describes the commencement of thermal decomposition of the polyolefin sample in a dynamic experiment. These dynamic experiments are carried out in open aluminium crucibles at a heating rate of 10°C/min and at an initial temperature of 30°C in a normal atmosphere. For the temperature range up to 260°C, the calibration standard used is indium (melting point $T_s = 156.8^\circ\text{C}$; enthalpy of melting $\Delta H_s = 26.8 \text{ J/g}$). The higher the oxidation temperature (T_{ox}), the better the polyolefins are stabilized and the more stable the polyolefins are to extracting water which is in permanent contact with the polyolefins. The results are summarized in Tables 4 and 5.

Table 4: Extraction experiments in water at 95°C

Extraction duration (hours)	Oxidation temperature (T_{ox}) in °C		
	Example 1a	Example 1b	Example 1c
0	256.9	255.1	247.4
2112	231.9	247.3	242.7
4272	223.5	245.6	241.1
7488	220.1	243.1	235.2
16032	214.4	236.2	227.2

Table 5: Extraction experiments with water at 105°C

Extraction duration (hours)	Oxidation temperature (T _{ox}) in °C		
	Example 1a	Example 1b	Example 1c
0	256.9	255.1	247.4
1915	237.4	240.9	238.1
4080	216.8	231.5	234.5
6000	216.5	222.2	230.5

Example 2: Stability of polyethylene which is in permanent contact with water and which has been stabilized by means of a component (b) and a component (c)(iii).

The stabilizers shown in Table 6 are incorporated into the medium-density polyethylene (PE-MD) analogously to Example 1 (Examples 2a, 2b and 2c).

Table 6:

Example	Stabilizer	Amount (% by wt.)	Molar mass (g/mol)	m.p. (°C)
Example 2a	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.10	1178	110-125
Example 2b	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Chimassorb 944LD ^{c)}	0.20	>2500	120-150
Example 2c	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Chimassorb 119FL/10 ^{d)}	0.20	2286	115-150

a) Irgafos[®] 168 (Ciba-Geigy) is tris(2,4-di-tert-butylphenyl) phosphite.

- b) Irganox[®]1010 (Ciba-Geigy) is the pentaerythritol ester of 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid.
- c) Chimassorb[®]944LD (Ciba-Geigy) denotes the linear or cyclic condensation products prepared from N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine.
- d) Chimassorb[®]119FL/10 (Ciba-Geigy) denotes a condensation product prepared from 2-chloro-4,6-di(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane.

The stabilized polyethylene test sheets are subjected, analogously to Example 1, to the water extraction conditions described in Example 1 at 95°C for up to 16,030 hours (668 days). When the extraction experiments are complete, the tear strength in megapascals (MPa) of the test sheets is determined. The tear strength is measured in accordance with DIN 53504 using an S2 standard rod. The tensile tests are carried out at room temperature at the earliest 24 hours after the respective sample has been removed from the water bath. The take-off rate is 200 mm/minute. The higher the tear strength value, the better the polyolefins are stabilized and the more stable the polyolefins are to extracting water which is in permanent contact with the polyolefins. The results are summarized in Table 7.

Table 7: Extraction experiments with water at 95°C

Extraction duration (hours)	Tear strength in MPa		
	Example 2a	Example 2b	Example 2c
0	36.3	38.8	35.5
2034	24.6	37.1	33.0
5708	20.3	35.2	30.2
7487	18.6	30.7	28.4
16030	16.9	27.7	19.9

Example 3: Stability of polyethylene which is in permanent contact with water and which has been stabilized by means of a component (b) and a component (c)(iii).

The stabilizers shown in Table 8 are incorporated into the medium-density polyethylene analogously to Example 1.

Table 8:

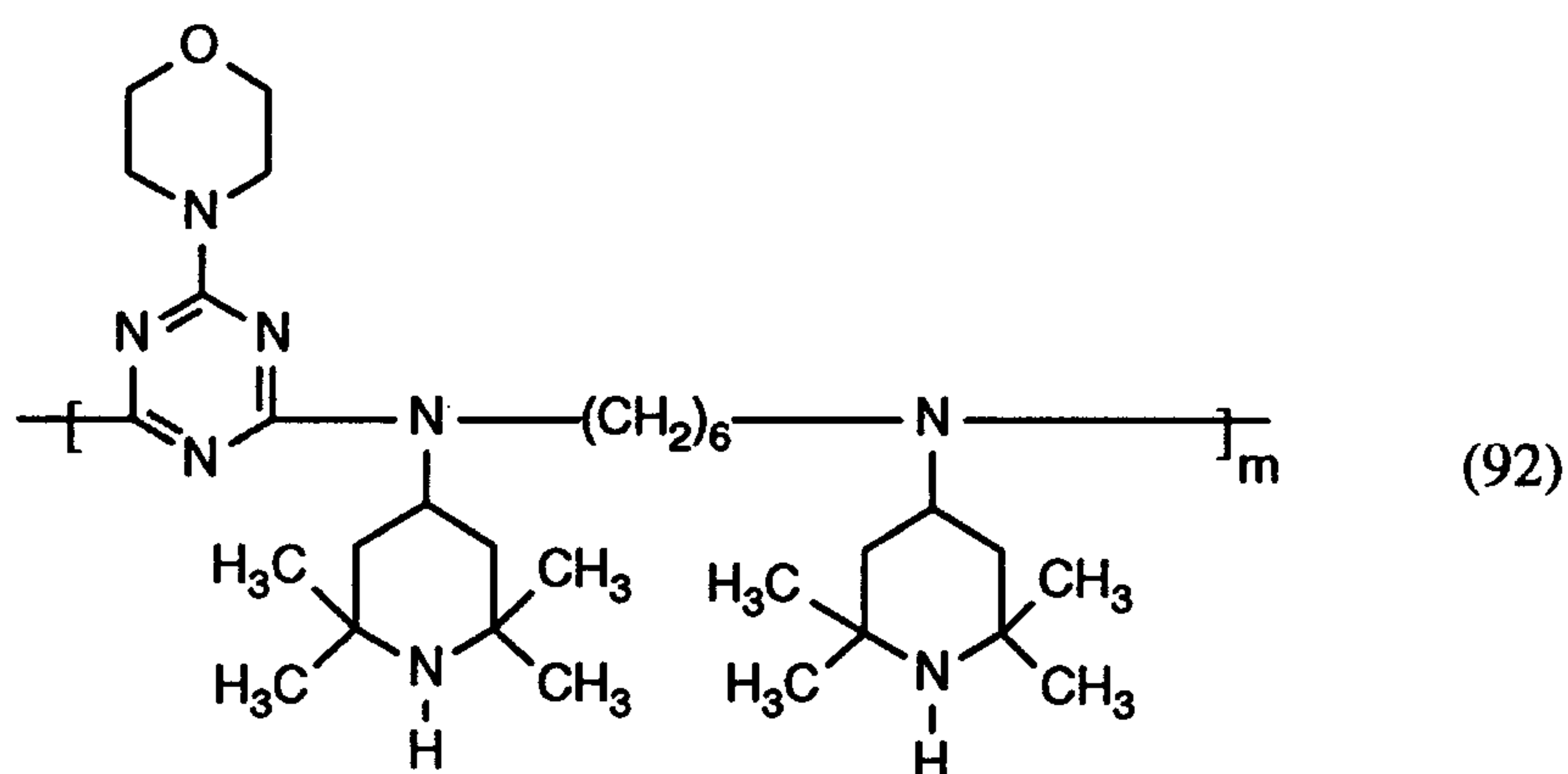
Example	Stabilizer	Amount (% by wt.)	Molar mass (g/mol)	m.p. (°C)
Example 3a	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.10	1178	110-125
Example 3b	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Tinuvin 622 ^{c)}	0.20	>2500	55-70
Example 3c	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Cyasorb 3346 ^{d)}	0.20	1500-1800	110-130
Example 3d	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Hostavin N30 ^{e)}	0.20	>1500	100-130
Example 3e	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Uvasorb HA 88 ^{f)}	0.20	3300	120-150
Example 3f	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Dastib 1082 ^{g)}	0.20	2970	162-181
Example 3g	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Uvinul 5050 ^{h)}	0.20	3500	95-125

Table 8: (continuation)

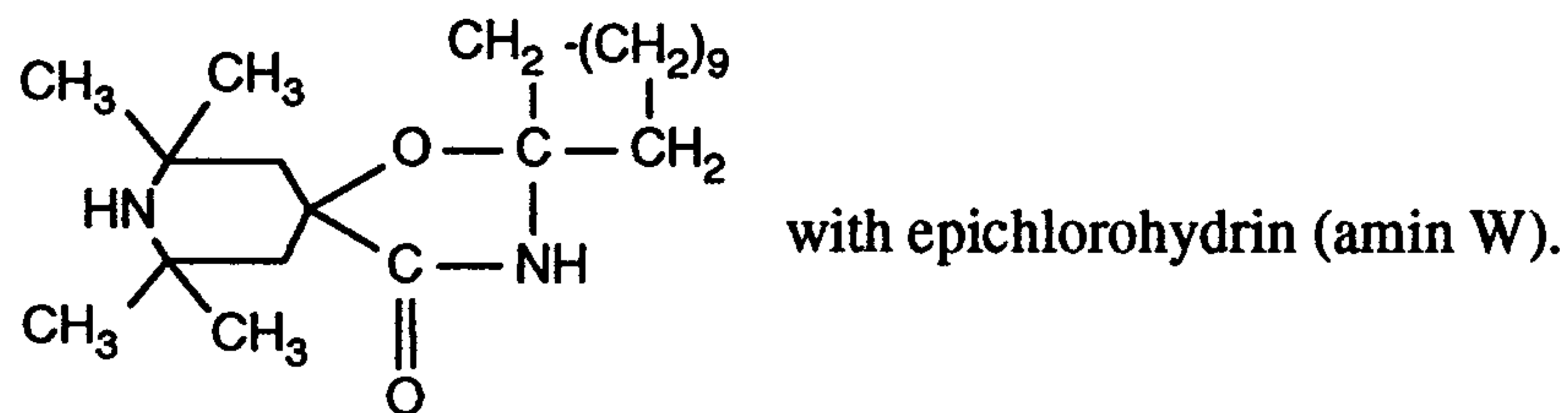
Example	Stabilizer	Amount (% by wt.)	Molar mass (g/mol)	m.p. (°C)
Example 3h	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	MARK LA 63 ⁱ⁾	0.20	2000	80-90
Example 3i	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	MARK LA 68 ^{j)}	0.20	1900	70-80
Example 3j	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Uvasil 299 ^{k)}	0.20	1100-2500	
Example 3k	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Lichtschtzstoff UV-31 ^{l)}	0.20	2580	100-125
Example 3l	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Chimassorb 944 ^{m)}	0.20	2580	100-125
Example 3m	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Chimassorb 119 FL/10 ⁿ⁾	0.20	2580	100-125

a) Irgafos[®] 168 (Ciba-Geigy) is tris(2,4-di-tert-butylphenyl)phosphite.

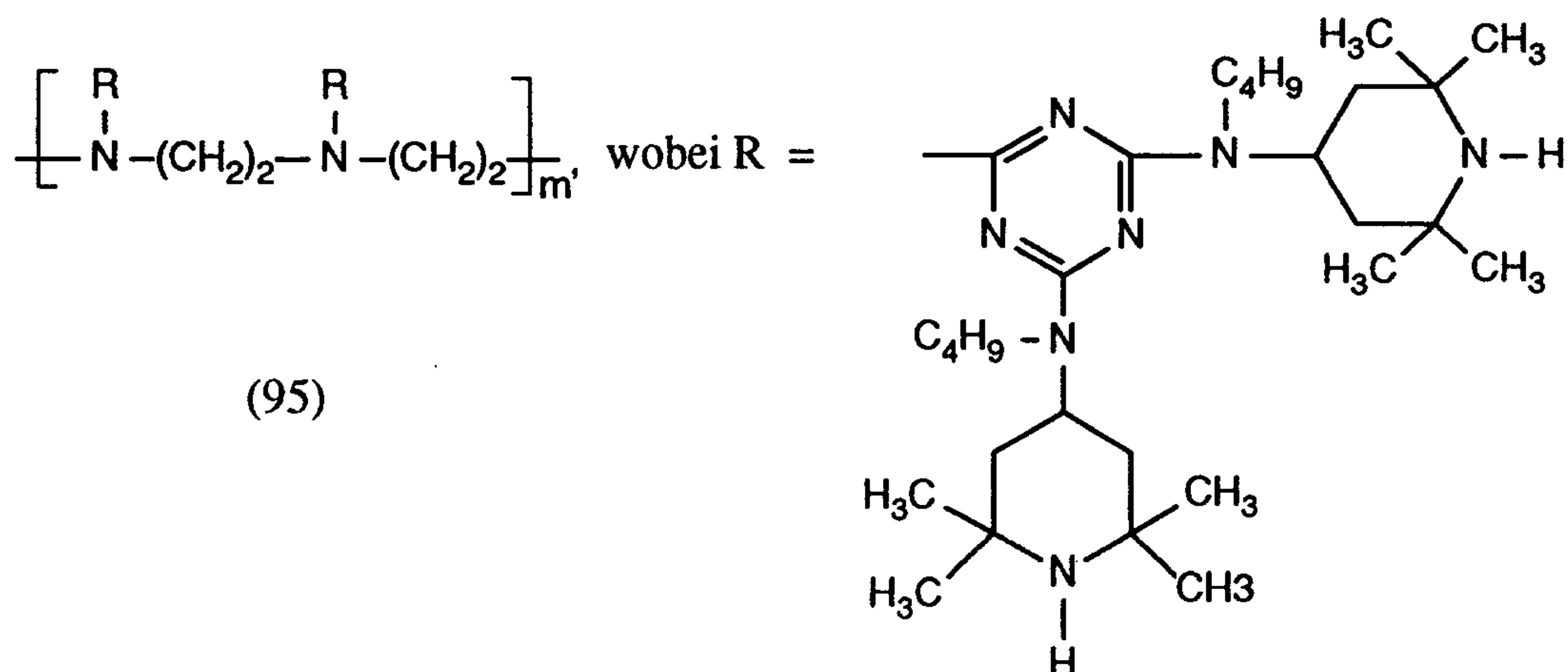
- b) Irganox[®] 1010 (Ciba-Geigy) is the pentaerythrol ester of 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid.
- c) Tinuvin[®] 622 (Ciba-Geigy) is poly-(N-β-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidyl succinate).
- d) Cyasorb[®] UV 3346 (Cytec) is a compound of the formula 92.



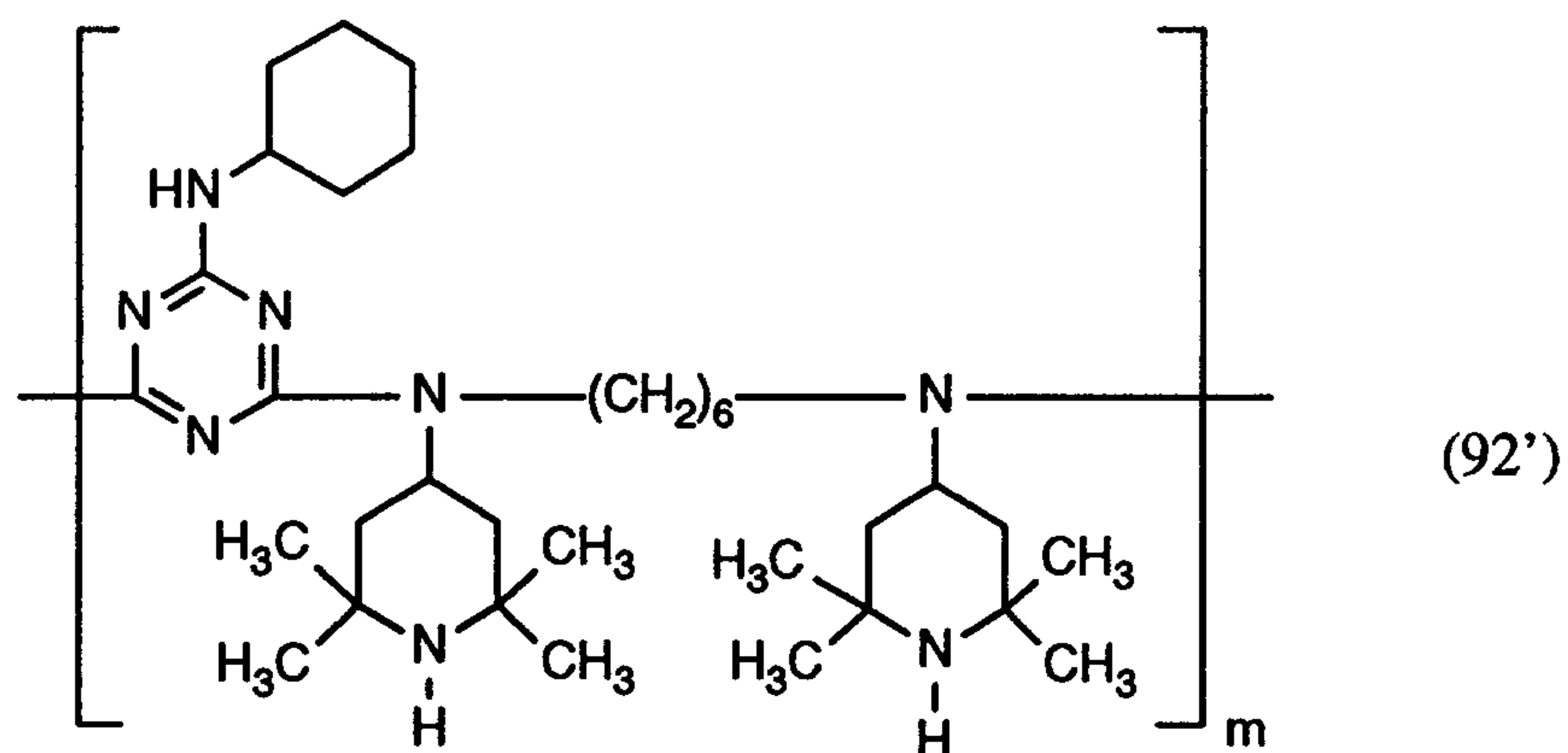
- e) Hostavin[®] N30 (Hoechst) is a reaction product of the compound the formula



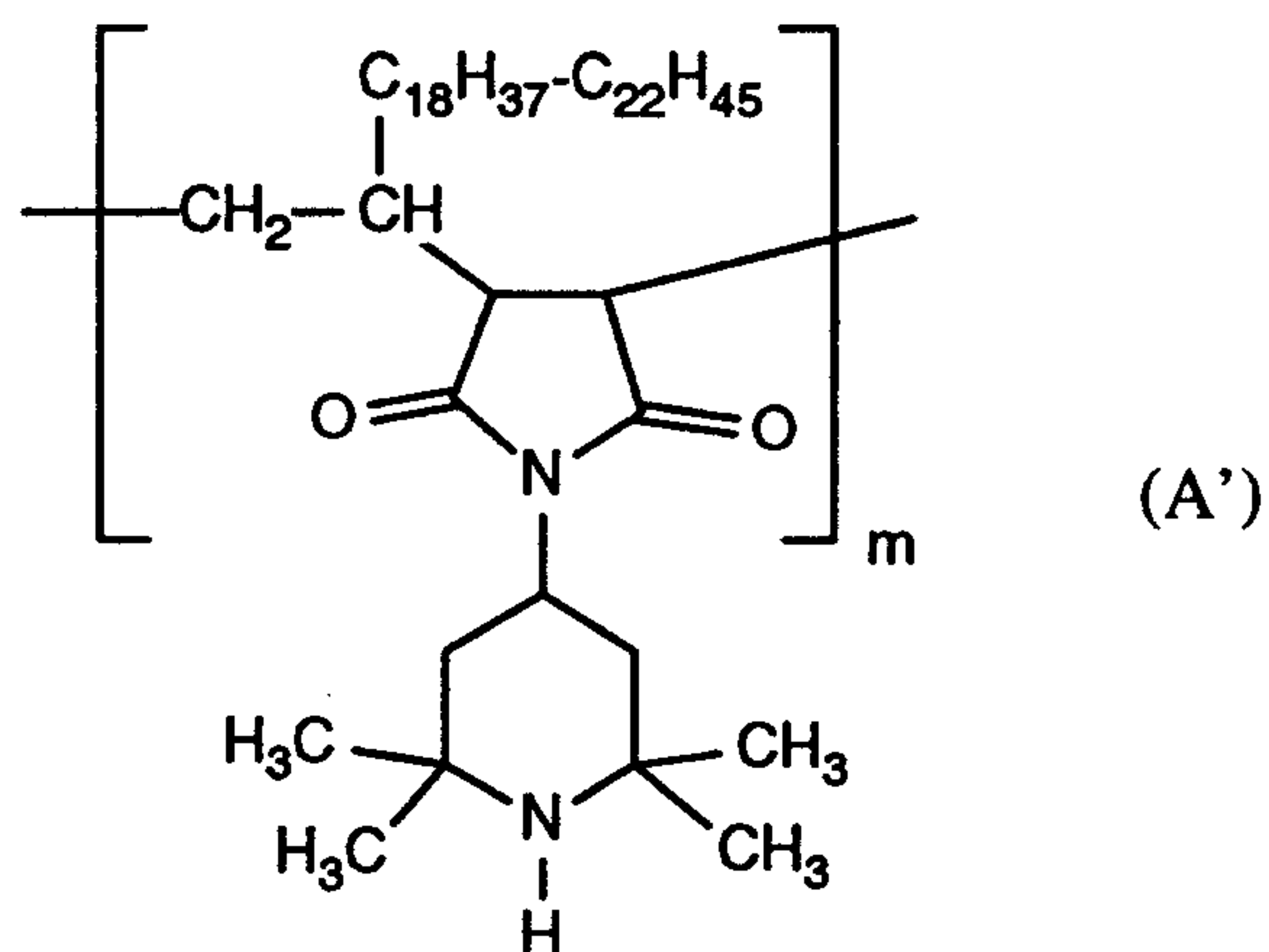
- f) Uvasorb[®] HA 88 (Sigma) is a compound of the formula 95.



g) Dastib[®]1082 (Slovakia) is a compound of the formula 92'.



h) Uvinul[®]5050 (BASF) is a compound of the formula A'.



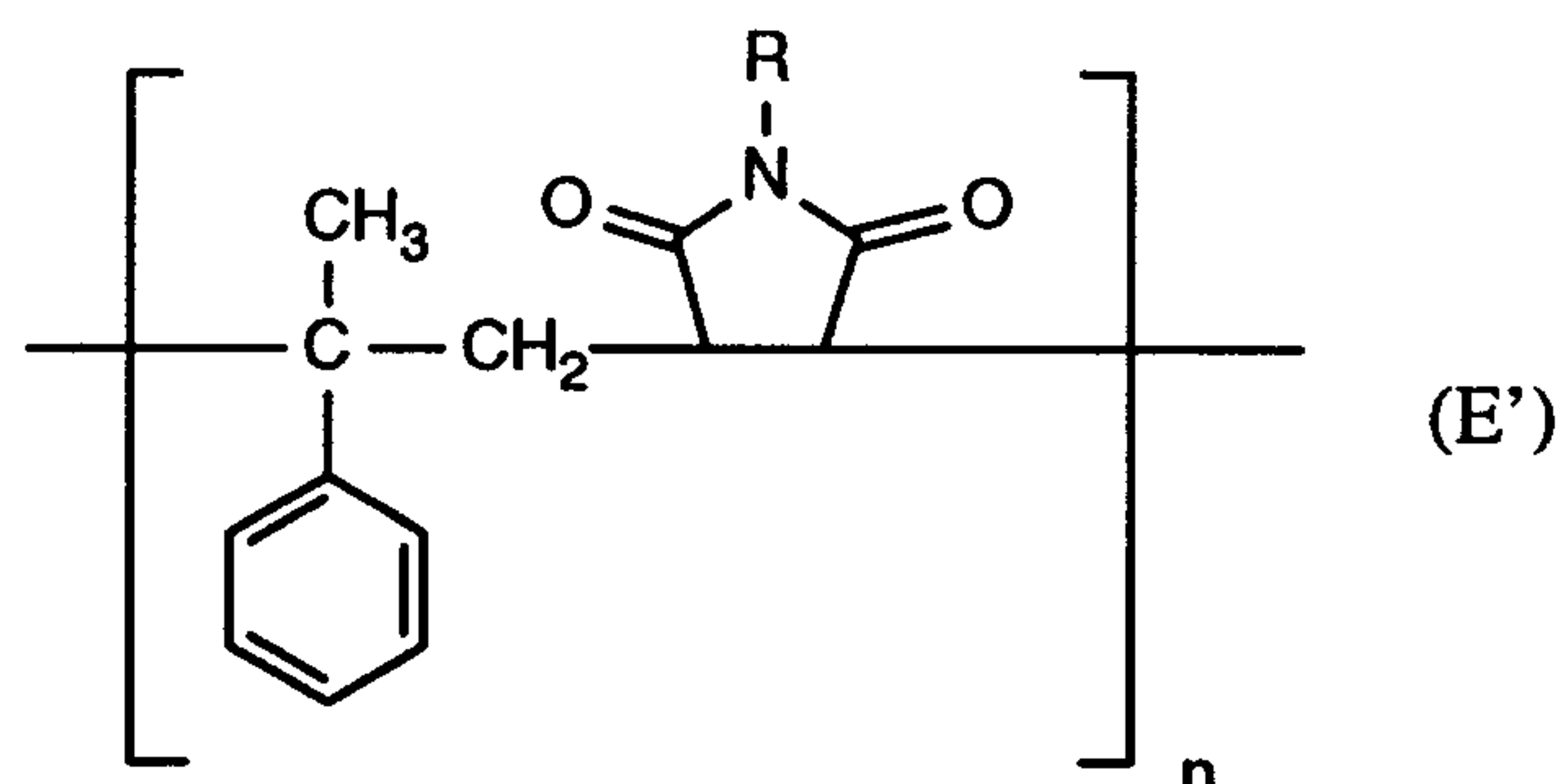
i) MARK[®]LA 63 (Asahi Denka) is a compound of the formula B'.

*C(=O)CC(C(=O)OC1C(C(C(C1)N)C)C)CC(=O)OCC(C)(C)C1C2C(C(C(C2)N)C)C3C(C(C(C3)N)C)C4C(C(C(C4)N)C)C5C(C(C(C5)N)C)C6C(C(C(C6)N)C)C7C(C(C(C7)N)C)C8C(C(C(C8)N)C)C9C(C(C(C9)N)C)C10C(C(C(C10)N)C)C11C(C(C(C11)N)C)C12C(C(C(C12)N)C)C13C(C(C(C13)N)C)C14C(C(C(C14)N)C)C15C(C(C(C15)N)C)C16C(C(C(C16)N)C)C17C(C(C(C17)N)C)C18C(C(C(C18)N)C)C19C(C(C(C19)N)C)C20C(C(C(C20)N)C)C21C(C(C(C21)N)C)C22C(C(C(C22)N)C)C23C(C(C(C23)N)C)C24C(C(C(C24)N)C)C25C(C(C(C25)N)C)C26C(C(C(C26)N)C)C27C(C(C(C27)N)C)C28C(C(C(C28)N)C)C29C(C(C(C29)N)C)C30C(C(C(C30)N)C)C31C(C(C(C31)N)C)C32C(C(C(C32)N)C)C33C(C(C(C33)N)C)C34C(C(C(C34)N)C)C35C(C(C(C35)N)C)C36C(C(C(C36)N)C)C37C(C(C(C37)N)C)C38C(C(C(C38)N)C)C39C(C(C(C39)N)C)C40C(C(C(C40)N)C)C41C(C(C(C41)N)C)C42C(C(C(C42)N)C)C43C(C(C(C43)N)C)C44C(C(C(C44)N)C)C45C(C(C(C45)N)C)C46C(C(C(C46)N)C)C47C(C(C(C47)N)C)C48C(C(C(C48)N)C)C49C(C(C(C49)N)C)C50C(C(C(C50)N)C)C51C(C(C(C51)N)C)C52C(C(C(C52)N)C)C53C(C(C(C53)N)C)C54C(C(C(C54)N)C)C55C(C(C(C55)N)C)C56C(C(C(C56)N)C)C57C(C(C(C57)N)C)C58C(C(C(C58)N)C)C59C(C(C(C59)N)C)C60C(C(C(C60)N)C)C61C(C(C(C61)N)C)C62C(C(C(C62)N)C)C63C(C(C(C63)N)C)C64C(C(C(C64)N)C)C65C(C(C(C65)N)C)C66C(C(C(C66)N)C)C67C(C(C(C67)N)C)C68C(C(C(C68)N)C)C69C(C(C(C69)N)C)C70C(C(C(C70)N)C)C71C(C(C(C71)N)C)C72C(C(C(C72)N)C)C73C(C(C(C73)N)C)C74C(C(C(C74)N)C)C75C(C(C(C75)N)C)C76C(C(C(C76)N)C)C77C(C(C(C77)N)C)C78C(C(C(C78)N)C)C79C(C(C(C79)N)C)C80C(C(C(C80)N)C)C81C(C(C(C81)N)C)C82C(C(C(C82)N)C)C83C(C(C(C83)N)C)C84C(C(C(C84)N)C)C85C(C(C(C85)N)C)C86C(C(C(C86)N)C)C87C(C(C(C87)N)C)C88C(C(C(C88)N)C)C89C(C(C(C89)N)C)C90C(C(C(C90)N)C)C91C(C(C(C91)N)C)C92C(C(C(C92)N)C)C93C(C(C(C93)N)C)C94C(C(C(C94)N)C)C95C(C(C(C95)N)C)C96C(C(C(C96)N)C)C97C(C(C(C97)N)C)C98C(C(C(C98)N)C)C99C(C(C(C99)N)C)C100C(C(C(C100)N)C)C101C(C(C(C101)N)C)C102C(C(C(C102)N)C)C103C(C(C(C103)N)C)C104C(C(C(C104)N)C)C105C(C(C(C105)N)C)C106C(C(C(C106)N)C)C107C(C(C(C107)N)C)C108C(C(C(C108)N)C)C109C(C(C(C109)N)C)C110C(C(C(C110)N)C)C111C(C(C(C111)N)C)C112C(C(C(C112)N)C)C113C(C(C(C113)N)C)C114C(C(C(C114)N)C)C115C(C(C(C115)N)C)C116C(C(C(C116)N)C)C117C(C(C(C117)N)C)C118C(C(C(C118)N)C)C119C(C(C(C119)N)C)C120C(C(C(C120)N)C)C121C(C(C(C121)N)C)C122C(C(C(C122)N)C)C123C(C(C(C123)N)C)C124C(C(C(C124)N)C)C125C(C(C(C125)N)C)C126C(C(C(C126)N)C)C127C(C(C(C127)N)C)C128C(C(C(C128)N)C)C129C(C(C(C129)N)C)C130C(C(C(C130)N)C)C131C(C(C(C131)N)C)C132C(C(C(C132)N)C)C133C(C(C(C133)N)C)C134C(C(C(C134)N)C)C135C(C(C(C135)N)C)C136C(C(C(C136)N)C)C137C(C(C(C137)N)C)C138C(C(C(C138)N)C)C139C(C(C(C139)N)C)C140C(C(C(C140)N)C)C141C(C(C(C141)N)C)C142C(C(C(C142)N)C)C143C(C(C(C143)N)C)C144C(C(C(C144)N)C)C145C(C(C(C145)N)C)C146C(C(C(C146)N)C)C147C(C(C(C147)N)C)C148C(C(C(C148)N)C)C149C(C(C(C149)N)C)C150C(C(C(C150)N)C)C151C(C(C(C151)N)C)C152C(C(C(C152)N)C)C153C(C(C(C153)N)C)C154C(C(C(C154)N)C)C155C(C(C(C155)N)C)C156C(C(C(C156)N)C)C157C(C(C(C157)N)C)C158C(C(C(C158)N)C)C159C(C(C(C159)N)C)C160C(C(C(C160)N)C)C161C(C(C(C161)N)C)C162C(C(C(C162)N)C)C163C(C(C(C163)N)C)C164C(C(C(C164)N)C)C165C(C(C(C165)N)C)C166C(C(C(C166)N)C)C167C(C(C(C167)N)C)C168C(C(C(C168)N)C)C169C(C(C(C169)N)C)C170C(C(C(C170)N)C)C171C(C(C(C171)N)C)C172C(C(C(C172)N)C)C173C(C(C(C173)N)C)C174C(C(C(C174)N)C)C175C(C(C(C175)N)C)C176C(C(C(C176)N)C)C177C(C(C(C177)N)C)C178C(C(C(C178)N)C)C179C(C(C(C179)N)C)C180C(C(C(C180)N)C)C181C(C(C(C181)N)C)C182C(C(C(C182)N)C)C183C(C(C(C183)N)C)C184C(C(C(C184)N)C)C185C(C(C(C185)N)C)C186C(C(C(C186)N)C)C187C(C(C(C187)N)C)C188C(C(C(C188)N)C)C189C(C(C(C189)N)C)C190C(C(C(C190)N)C)C191C(C(C(C191)N)C)C192C(C(C(C192)N)C)C193C(C(C(C193)N)C)C194C(C(C(C194)N)C)C195C(C(C(C195)N)C)C196C(C(C(C196)N)C)C197C(C(C(C197)N)C)C198C(C(C(C198)N)C)C199C(C(C(C199)N)C)C200C(C(C(C200)N)C)C201C(C(C(C201)N)C)C202C(C(C(C202)N)C)C203C(C(C(C203)N)C)C204C(C(C(C204)N)C)C205C(C(C(C205)N)C)C206C(C(C(C206)N)C)C207C(C(C(C207)N)C)C208C(C(C(C208)N)C)C209C(C(C(C209)N)C)C210C(C(C(C210)N)C)C211C(C(C(C211)N)C)C212C(C(C(C212)N)C)C213C(C(C(C213)N)C)C214C(C(C(C214)N)C)C215C(C(C(C215)N)C)C216C(C(C(C216)N)C)C217C(C(C(C217)N)C)C218C(C(C(C218)N)C)C219C(C(C(C219)N)C)C220C(C(C(C220)N)C)C221C(C(C(C221)N)C)C222C(C(C(C222)N)C)C223C(C(C(C223)N)C)C224C(C(C(C224)N)C)C225C(C(C(C225)N)C)C226C(C(C(C226)N)C)C227C(C(C(C227)N)C)C228C(C(C(C228)N)C)C229C(C(C(C229)N)C)C230C(C(C(C230)N)C)C231C(C(C(C231)N)C)C232C(C(C(C232)N)C)C233C(C(C(C233)N)C)C234C(C(C(C234)N)C)C235C(C(C(C235)N)C)C236C(C(C(C236)N)C)C237C(C(C(C237)N)C)C238C(C(C(C238)N)C)C239C(C(C(C239)N)C)C240C(C(C(C240)N)C)C241C(C(C(C241)N)C)C242C(C(C(C242)N)C)C243C(C(C(C243)N)C)C244C(C(C(C244)N)C)C245C(C(C(C245)N)C)C246C(C(C(C246)N)C)C247C(C(C(C247)N)C)C248C(C(C(C248)N)C)C249C(C(C(C249)N)C)C250C(C(C(C250)N)C)C251C(C(C(C251)N)C)C252C(C(C(C252)N)C)C253C(C(C(C253)N)C)C254C(C(C(C254)N)C)C255C(C(C(C255)N)C)C256C(C(C(C256)N)C)C257C(C(C(C257)N)C)C258C(C(C(C258)N)C)C259C(C(C(C259)N)C)C260C(C(C(C260)N)C)C261C(C(C(C261)N)C)C262C(C(C(C262)N)C)C263C(C(C(C263)N)C)C264C(C(C(C264)N)C)C265C(C(C(C265)N)C)C266C(C(C(C266)N)C)C267C(C(C(C267)N)C)C268C(C(C(C268

(C')

$$\left[\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si}-\text{O} \\ | \\ (\text{CH}_2)_3 \\ | \\ \text{O} \\ | \\ \text{C} \\ / \quad \backslash \\ \text{C} \quad \text{C} \\ / \quad \backslash \quad / \quad \backslash \\ \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{CH}_3 \quad \text{CH}_3 \\ | \\ \text{N} \\ | \\ \text{H} \end{array} \right]_m \quad (\text{D}')$$

- l) Lichtschutzstoff UV-31 (Leuna) is a compound of the formula E'



in which R is octadecyl or 2,2,6,6-tetramethyl-4-piperidyl.

- m) Chimassorb[®]944LD (Ciba-Geigy) denotes the linear or cyclic condensation products prepared from N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine.
- n) Chimassorb[®]119FL/10 (Ciba-Geigy) denotes a condensation product prepared from 2-chloro-4,6-di(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane.

The stabilized polyethylene test sheets are subjected, analogously to Example 1, to the water extraction conditions described in Example 1 at 95°C for up to 16,030 hours (668 days). When the extraction experiments are complete, the tear strength of the test sheets is determined in percent. The tear strength is measured in accordance with DIN 53504 using an S2 standard rod. The tensile tests are carried out at room temperature at the earliest 24 hours after the respective sample has been removed from the water bath. The take-off rate is 200 mm/minute. The higher the tear strength value, the better the polyolefins are stabilized and the more stable the polyolefins are to extracting water which is in permanent contact with the polyolefins. The results are summarized in Table 9.

Table 9: Extraction experiments with water at 95°C

Examples	Tear strength in percent after x hours of extraction				
	0 hour	2034 hours	5708 hours	7487 hours	16030 hours
Example 3a	840	651	592	598	581
Example 3b	845	675	642	601	601
Example 3c	841	762	678	685	620
Example 3d	835	775	766	671	615
Example 3e	836	681	634	645	617
Example 3f	840	721	635	631	618
Example 3g	842	702	688	679	619
Example 3h	839	684	627	623	621
Example 3i	838	681	679	595	619
Example 3j	846	709	635	625	624
Example 3k	850	711	630	576	622
Example 3l	851	842	805	801	723
Example 3m	849	815	733	702	675

Example 4: Stability of polyethylene which is in permanent contact with water and which has been stabilized by means of a component (b) and a component (c)(iii).

The stabilizers shown in Table 10 are incorporated into the medium-density polyethylene analogously to Example 1.

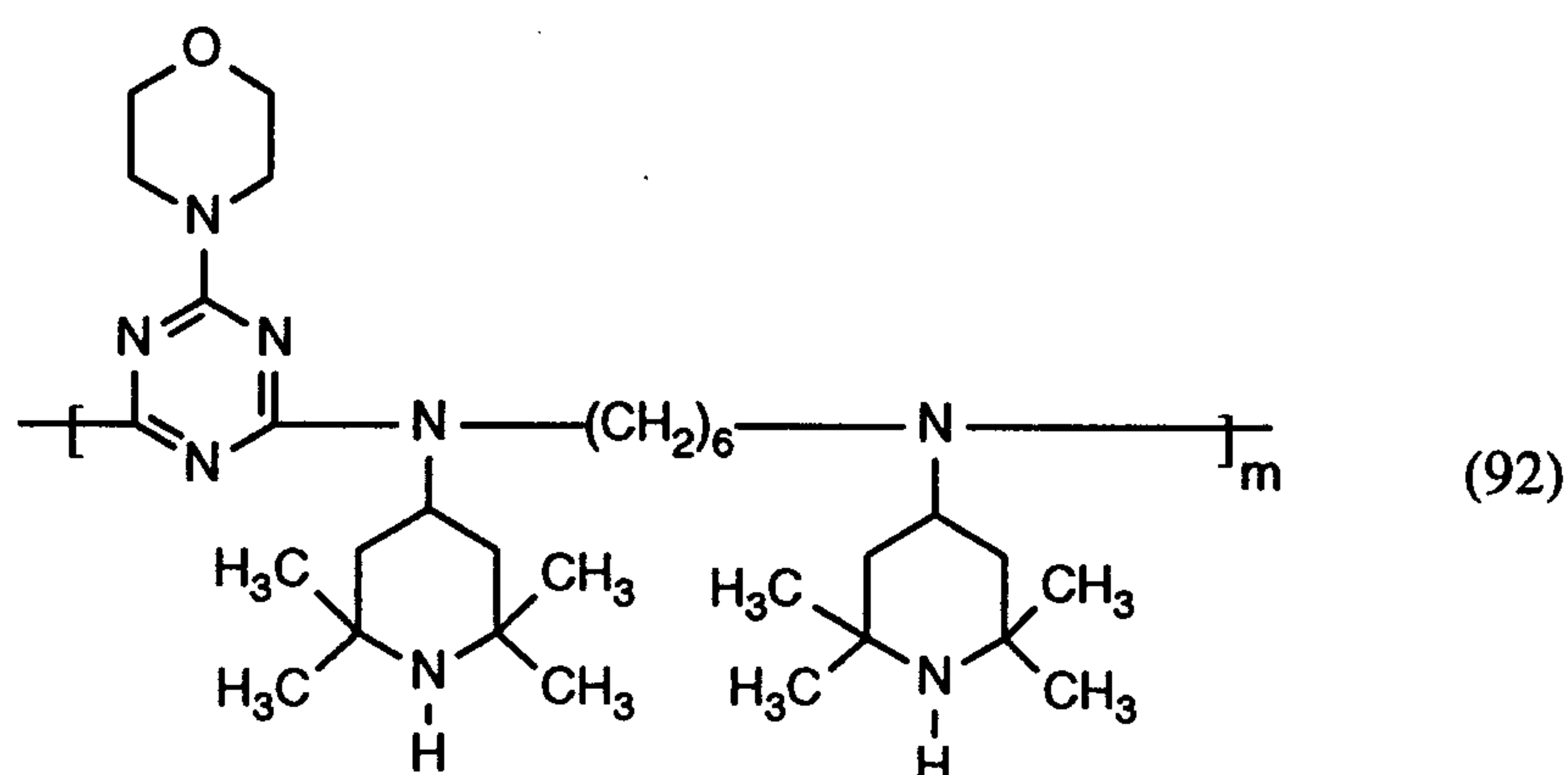
Table 10:

Example	Stabilizer	Amount (% by wt.)	Molar mass (g/mol)	m.p. (°C)
Example 4a	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.10	1178	110-125
Example 4b	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Chimassorb 944 ^{c)}	0.20	2580	100-125
Example 4c	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Cyasorb 3346 ^{d)}	0.20	1500-1800	110-130
Example 4d	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Uvasorb HA 88 ^{e)}	0.20	3300	120-150
Example 4e	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Hostavin N30 ^{f)}	0.20	>1500	100-130
Example 4f	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Uvinul 5050 ^{g)}	0.20	3500	95-125

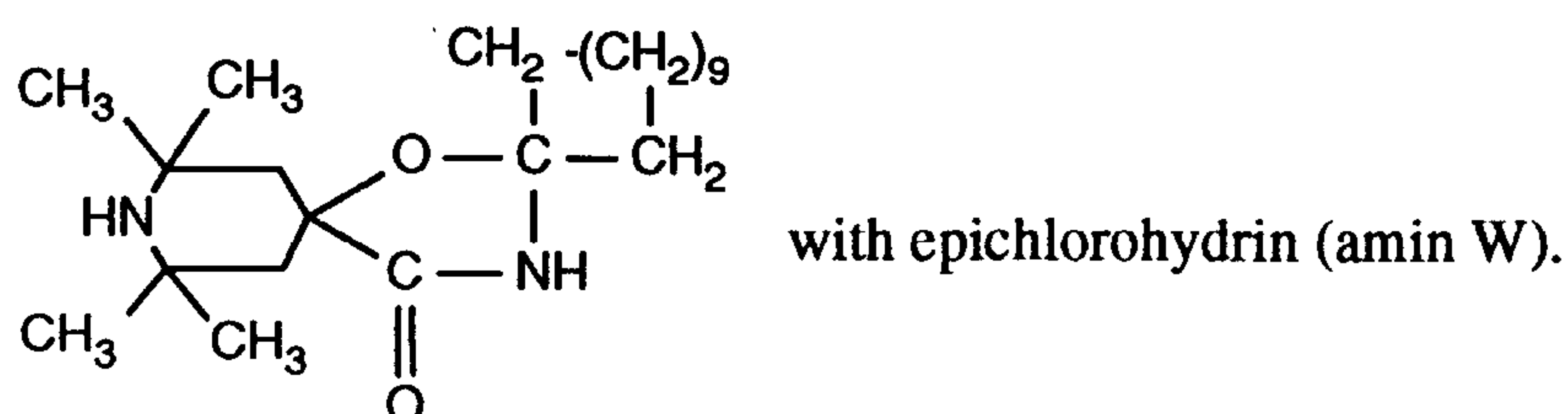
Table 10: (continuation)

Example	Stabilizer	Amount (% by wt.)	Molar mass (g/mol)	m.p. (°C)
Example 4g	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{b)}	0.05	1178	110-125
	Chimassorb 119 FL/10 ^{b)}	0.20	2580	100-125

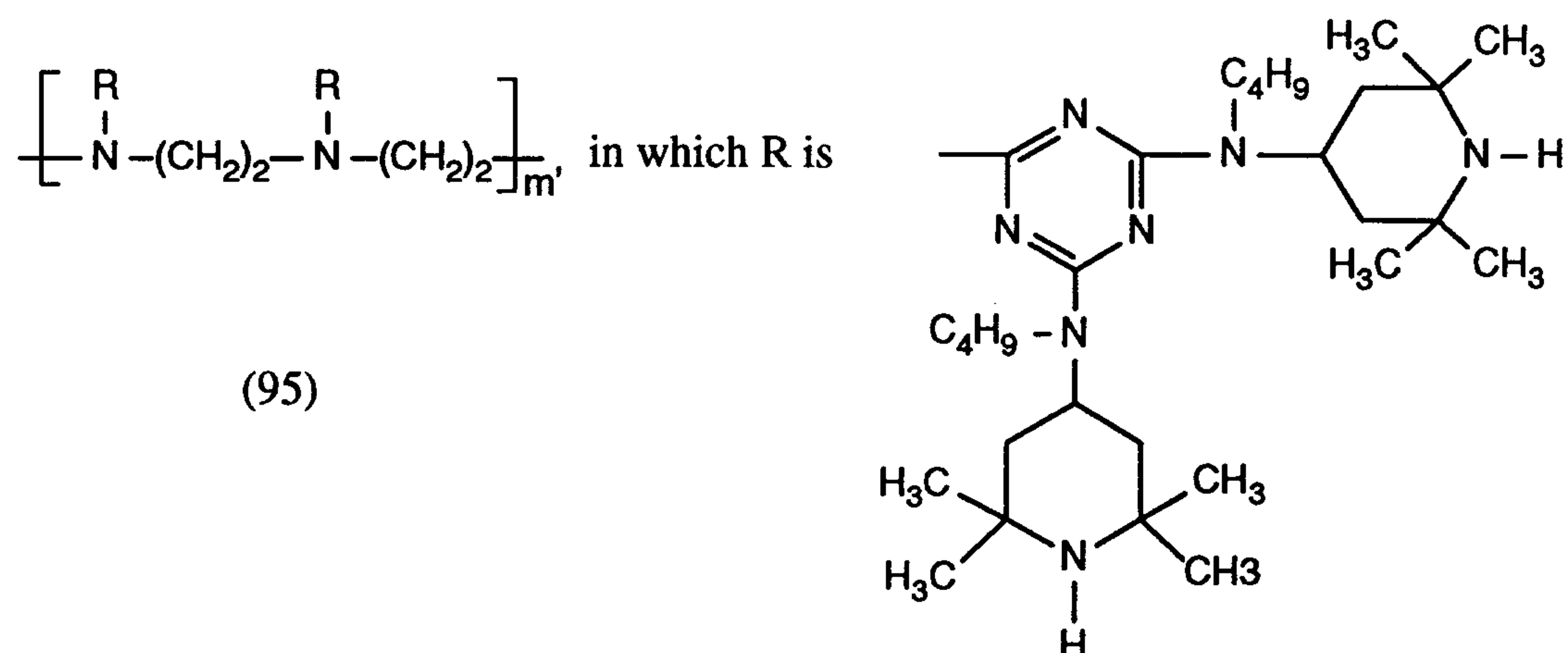
- a) Irgafos[®] 168 (Ciba-Geigy) is tris(2,4-di-tert-butylphenyl)phosphit.
- b) Irganox[®] 1010 (Ciba-Geigy) is the pentaerythritol ester of 3-(3,5-Di-tert-butyl-4-hydroxyphenyl)propionic acid.
- c) Chimassorb[®] 944 (Ciba-Geigy) denotes the linear or cyclic condensation products prepared from N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine.
- d) Cyasorb[®] UV 3346 (Cytec) is a compound of the formula 92.



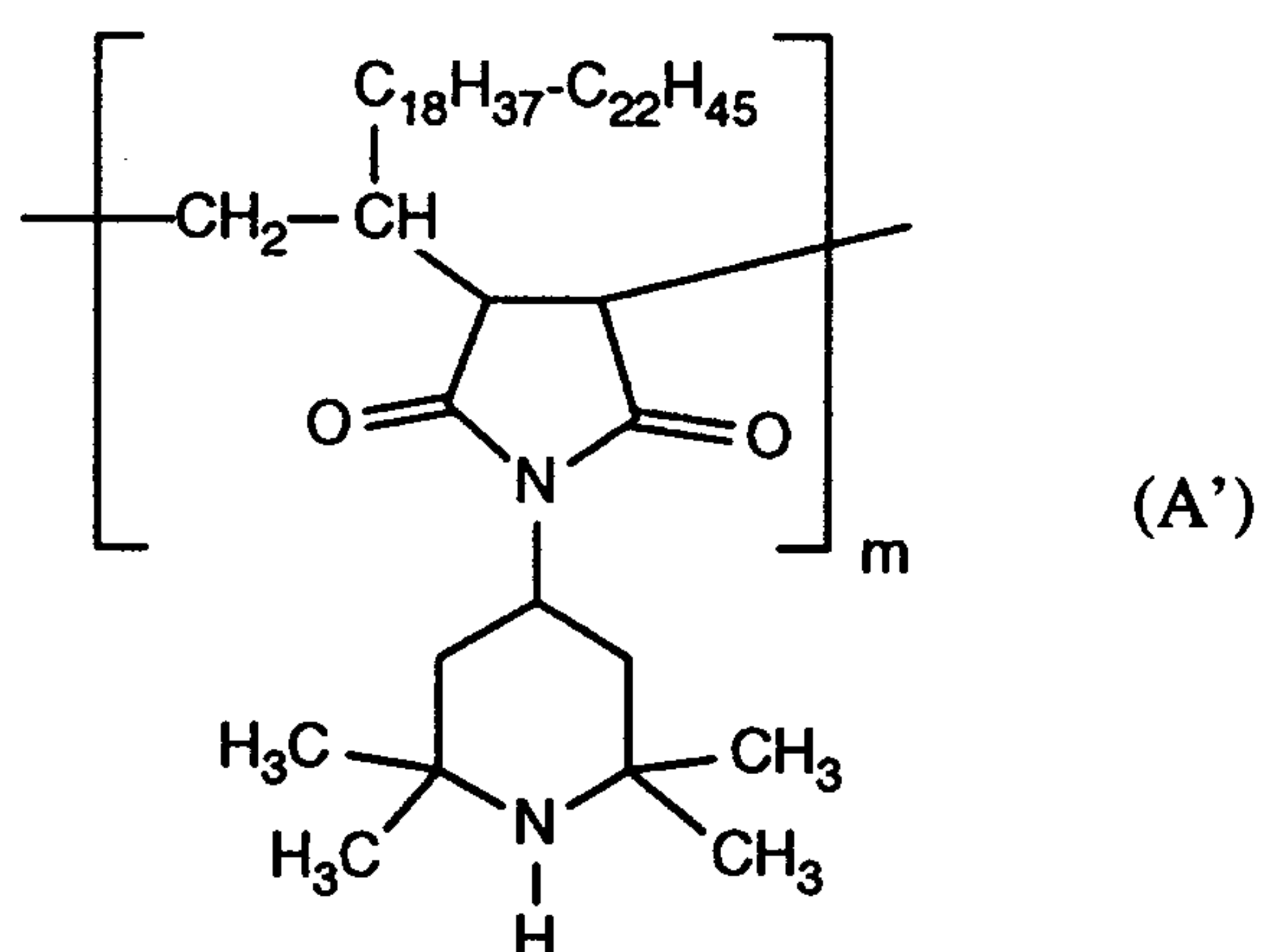
- e) Hostavin[®] N30 (Hoechst) is a reaction product of the compound the formula



- f) Uvasorb[®]HA 88 (Sigma) is a compound of the formula 95



- g) Uvinul[®]5050 (BASF) is a compound of the formula A'.



- h) Chimassorb[®]119 FL/10 (Ciba-Geigy) denotes a condensation product prepared from 2-chloro-4,6-di(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane.

The polyethylene was extruded by an extruder of the Maillefer type to form pipes with an outside diameter of 20 mm and a wall-thickness of 2 mm. The machine parameters for the preparation of the pipes are summarized in Table 11.

Table 11: Machine parameters for the prapartion of pipes

Cylinder temperature	185, 195, 210 und 220°C
Nozzle temperature	220, 200 und 190°C
Screw configuration	L/d = 25, d = 60 mm
Screw speed	56 rpm
Cooling agent	Water
Take-off speed	6 m/minute

The stability of the polyethylene pipes are measured at 105°C (inside of the pipe is water, outside of the pipe is air) and a hoop stress of 1.5 MPa in the inside compressive creep test according to DIN 53759. Under this low hoop stress a polyethylene pipe is decomposed by thermal-oxidative degradation. The higher the retention time value, the better the polyolefins are stabilized and the more stable the polyolefins are to extracting water which is in permanent contact with the polyolefins. The results are summarized in Table 12.

Table 12: Stability of pipes (inside water, outside air)

Examples	Retention time in hours at a hoop stress of 1,5 MPa
Example 4a	10005
Example 4b	13245
Example 4c	11968
Example 4d	11902
Example 4e	11858
Example 4f	12012
Example 4g	15521

Example 5: Stability of polyethylene which is in permanent contact with water and which has been stabilized by means of a component (b) and a component (c)(iii).

The stabilizers shown in Table 13 are incorporated into the medium-density polyethylene (PE-LLD, MFI at 230°C/2.16 kg = 1.0 g/10 minutes, density = 0.937 g/cm³) analogously to Example 1.

Table 13:

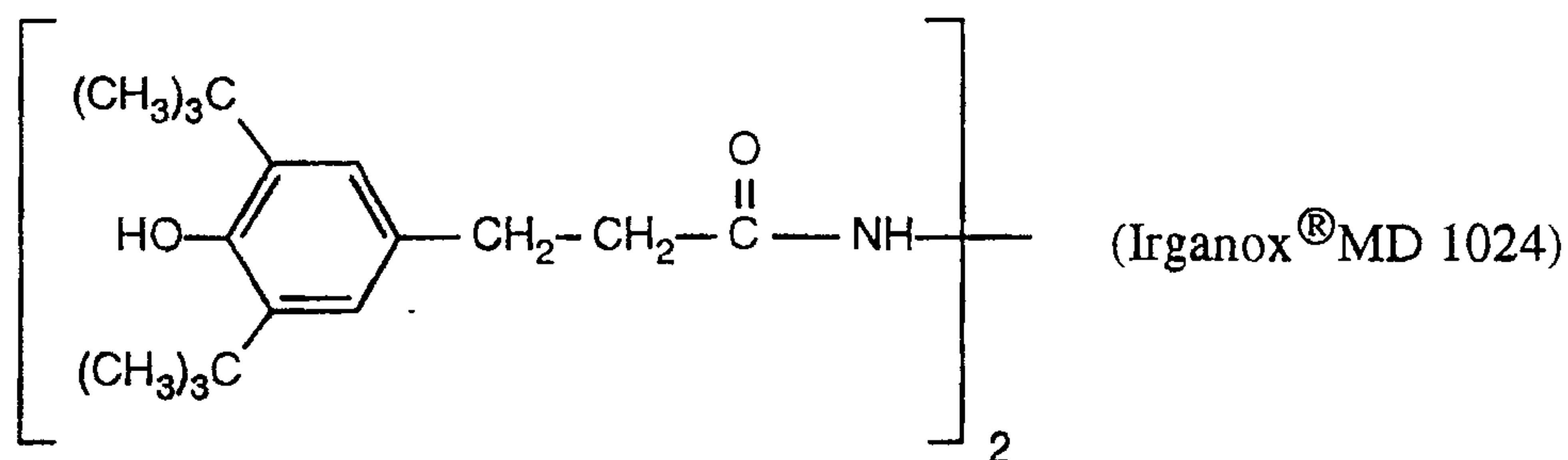
Example	Stabilizer	Amount (% by wt.)	Molar mass (g/mol)	m.p. (°C)
Example 5a	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox MD1024 ^{b)}	0.07	553	224-229
	Irganox 1330 ^{a)}	0.20	775	241-245
Example 5b	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox MD1024 ^{b)}	0.07	553	224-229
	Irganox 1330 ^{a)}	0.10	775	241-245
	Chimassorb 944 ^{a)}	0.10	2580	100-125
Example 5c	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox MD 1024 ^{b)}	0.07	553	224-229
	Irganox 1330 ^{a)}	0.10	775	241-245
	Chimassorb 119 FL/10 ^{a)}	0.10	2580	100-125

a) The chemical structures of Irgafos[®]168, Irganox[®]1330, Chimassorb[®]944 and Chimassorb[®]119 FL/10 are disclosed in the Examples 1, 2, 3 or 4.

b) Irganox[®]MD 1024 (Ciba-Geigy) is a compound of the formula

29276-401

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The stabilized polyethylene test sheets are subjected, analogously to Example 1, to the water extraction conditions described in Example 1 at 90°C for up to 12 months. When the extraction experiments are complete, the sheets are subjected to an oven aging in a circulating air oven at 110°C. The time until the polyolefins are embrittled is measured. The higher time until the polyolefins are embrittled, the better the polyolefins are stabilized and the more stable the polyolefins are to extracting water which is in permanent contact with the polyolefins. The results are summarized in Table 14.

Table 14: Oven ageing

Examples	Time until embrittlement in days
Example 5a	10
Example 5b	1071
Example 5c	1255

Example 6: Stability of polypropylene which is in permanent contact with water and which has been stabilized by means of a component (b) and a component (c)(iii).

The stabilizers shown in Table 15 are incorporated into the polypropylene rPP (statistical polypropylene copolymer, MFI at 230°C/2.16 kg = 0.8 g/10 minutes, density = 0.910 g/cm³) analogously to Example 1.

Table 15:

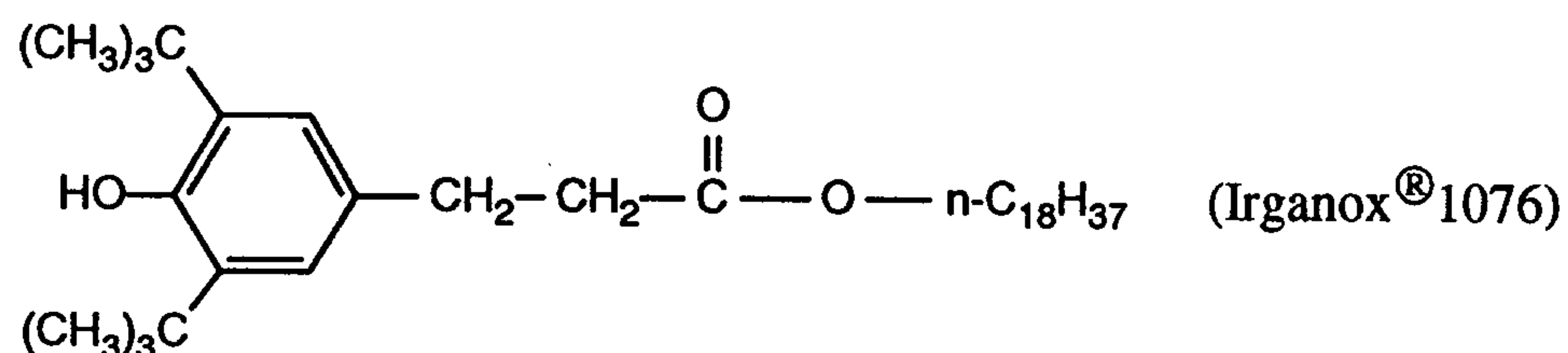
Examples	Stabilizer	Amount (% by wt.)	Molar mass (g/mol)	m.p. (°C)
Example 6a	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1076 ^{b)}	0.05	531	50-55
Example 6b	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1076 ^{b)}	0.05	531	50-55
	Chimassorb 944 ^{a)}	0.10	2580	100-125
Example 6c	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1076 ^{b)}	0.05	531	50-55
	Cyasorb 3346 ^{a)}	0.10	1500-1800	110-130
Example 6d	Irgafos PEPQ ^{c)}	0.10	991	85-110
	Irganox 1076 ^{b)}	0.05	531	50-55
	Chimassorb 944 ^{a)}	0.10	2580	100-125
Example 6e	Irgafos PEPQ ^{c)}	0.10	991	85-110
	Irganox 1076 ^{b)}	0.05	531	50-55
	Cyasorb 3346 ^{a)}	0.10	1500-1800	110-130
Example 6f	Irgafos 38 ^{d)}	0.10	514	89-92
	Irganox 1076 ^{b)}	0.05	531	50-55
	Chimassorb 944 ^{a)}	0.10	2580	100-125
Example 6g	Irgafos 38 ^{d)}	0.10	514	89-92
	Irganox 1076 ^{b)}	0.05	531	50-55
	Cyasorb 3346 ^{a)}	0.10	1500-1800	110-130

Table 15: (continuation)

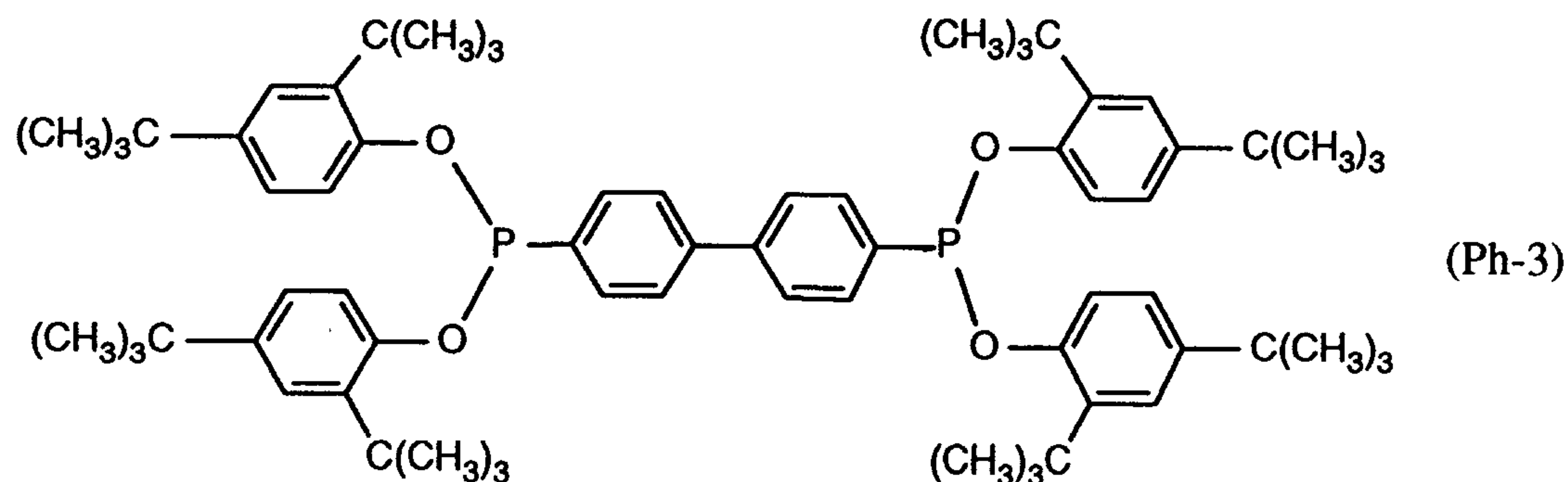
Examples	Stabilizer	Amount (% by wt.)	Molar mass (g/mol)	m.p. (°C)
Example 6h	Irgafos 12 ^{e)}	0.10	1465	205
	Irganox 1076 ^{b)}	0.05	531	50-55
	Chimassorb 944 ^{a)}	0.10	2580	100-125
Example 6i	Irgafos 12 ^{e)}	0.10	1465	205
	Irganox 1076 ^{b)}	0.05	531	50-55
	Cyasorb 3346 ^{a)}	0.10	1500-1800	110-130

a) The chemical structures of Irgafos[®]168, Chimassorb[®]944 and Cyasorb[®]3346 are disclosed in the Examples 1, 2, 3, 4 or 5.

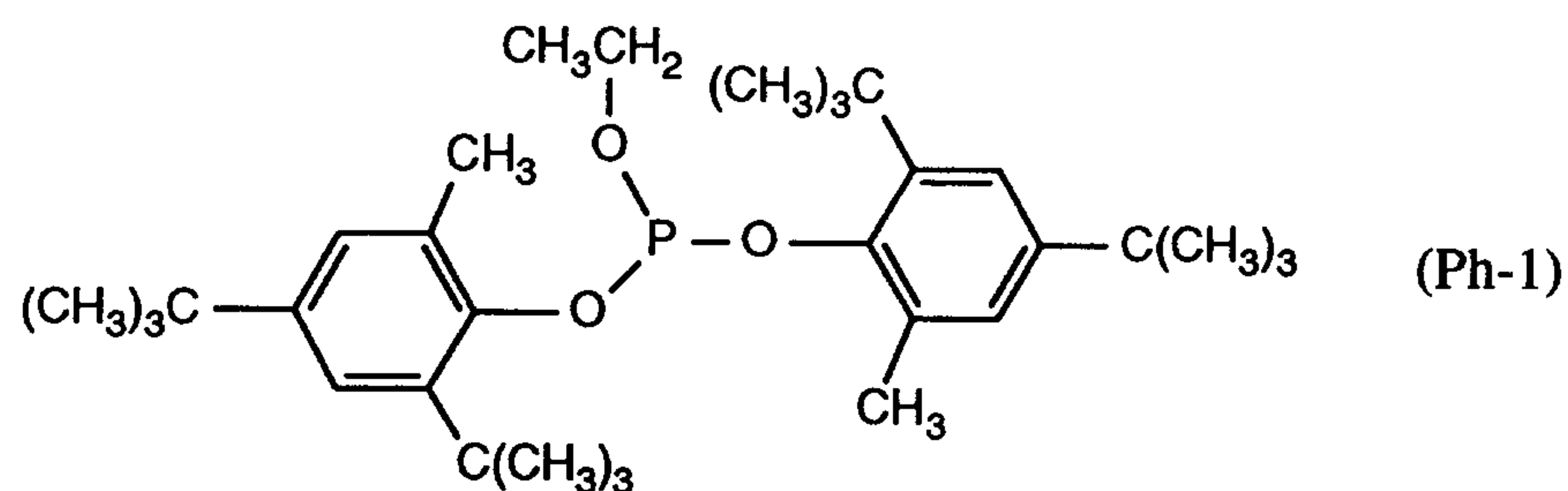
b) Irganox[®]1076 (Ciba-Geigy) is a compound of the formula



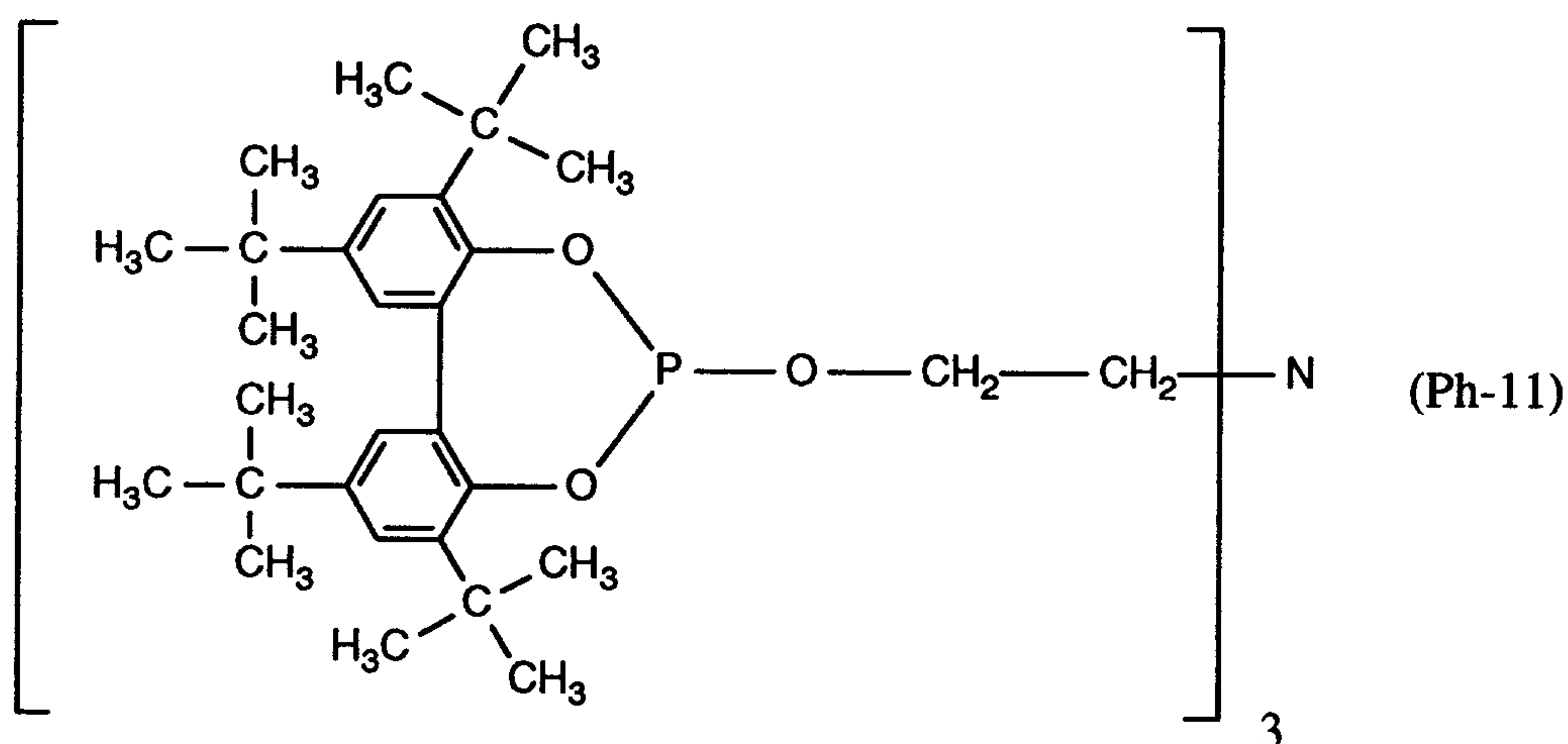
c) Irgafos[®]PEPQ (Ciba-Geigy) is a compound of the formula Ph-3.



d) Irgafos[®]38 (Ciba-Geigy) is a compound of the formula Ph-1.



e) Irgafos[®]12 (Ciba-Geigy) is a compound of the formula Ph-11.



The stabilized polypropylene test sheets are subjected, analogously to Example 1, to the water extraction conditions described in Example 1 at 98°C for up to 6 months. When the extraction experiments are complete, the sheets are subjected to an oven aging in a circulating air oven at 135°C. The time until the polyolefins are embrittled is measured. The higher time until the polyolefins are embrittled, the better the polyolefins are stabilized and the more stable the polyolefins are to extracting water which is in permanent contact with the polyolefins. The results are summarized in Table 16.

Table 16: Oven ageing

Examples	Time until embrittlement in days
Example 6a	5
Example 6b	33
Example 6c	36
Example 6d	32
Example 6e	36
Example 6f	38
Example 6g	42
Example 6h	35
Example 6i	34

Example 7: Stability of polypropylene which is in permanent contact with water and which has been stabilized by means of a component (b) and a component (c)(iii).

The stabilizers shown in Table 17 are incorporated into the polypropylene (MFI at 230°C/2.16 kg = 2.0 g/10 minutes, density = 0.905 g/cm³) analogously to Example 1.

Table 17:

Examples	Stabilizer	Amount (% by wt.)	Molar mass (g/mol)	m.p. (°C)
Example 7a	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{a)}	0.35	1178	110-125
Example 7b	Irgafos 168 ^{a)}	0.10	647	180-185
	Irganox 1010 ^{a)}	0.05	1178	110-125
	Chimassorb 119 FL/10 ^{a)}	0.35	2580	100-125

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- a) The chemical structures of Irgafos[®]168, Irganox[®]1010 and Chimassorb[®]119 FL/10 are disclosed in the Examples 1, 2, 3, 4, 5 or 6.

The stabilized polypropylene test sheets are subjected, analogously to Example 1, to the water extraction conditions described in Example 1 at 98°C for up to 6 months. When the extraction experiments are complete, the sheets are subjected to an oven aging in a circulating air oven at 120°C. The time until the polyolefins are embrittled is measured. The higher time until the polyolefins are embrittled, the better the polyolefins are stabilized and the more stable the polyolefins are to extracting water which is in permanent contact with the polyolefins. The results are summarized in Table 18.

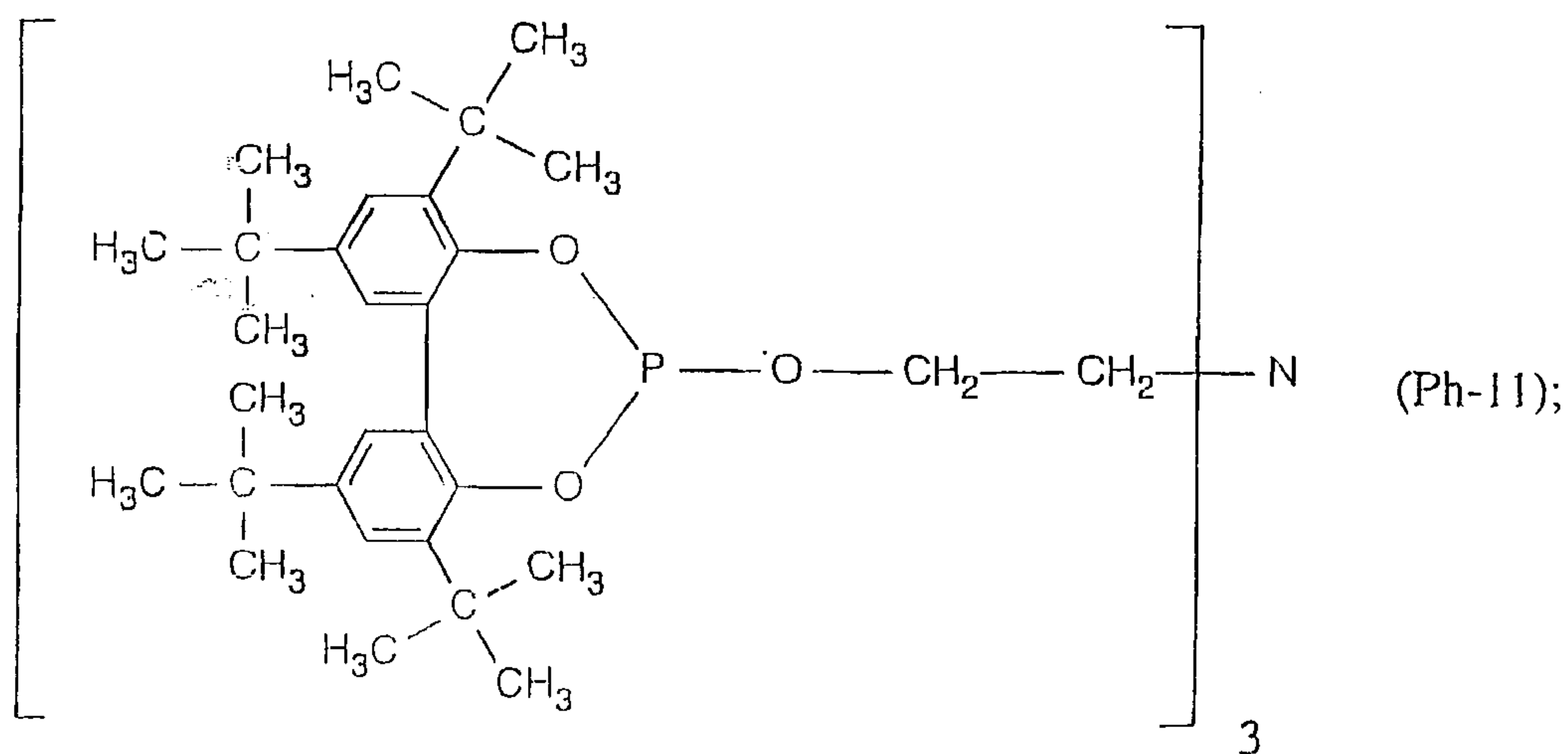
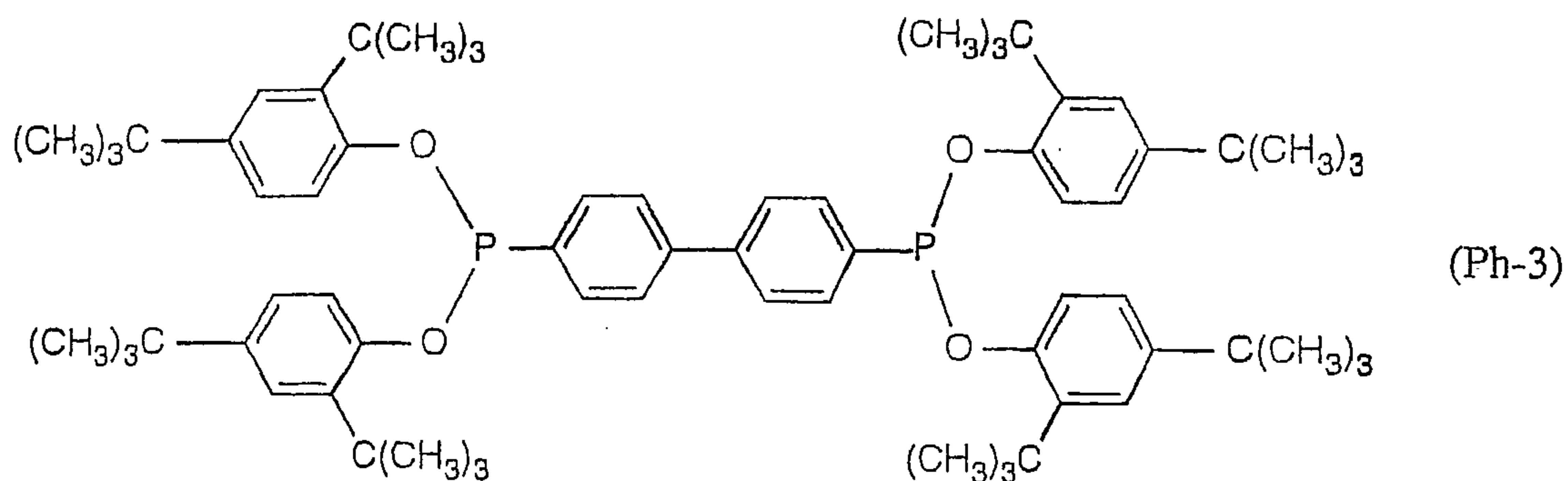
Table 18: Oven ageing

Examples	Time until embrittlement in days
Example 7a	215
Example 7b	504

CLAIMS:

1. A process for stabilizing a thick-walled polyolefin moulding which is in permanent contact with water, which comprises incorporating in or applying to said moulding a mixture of a component (b) in an amount of from 0.02 to 0.6 % based on the weight of the moulding, a component (c) in an amount of from 0.02 to 0.5 % based on the weight of the moulding and a component (d) in an amount of from 0.02 to 1.0 % based on the weight of the moulding, in which .

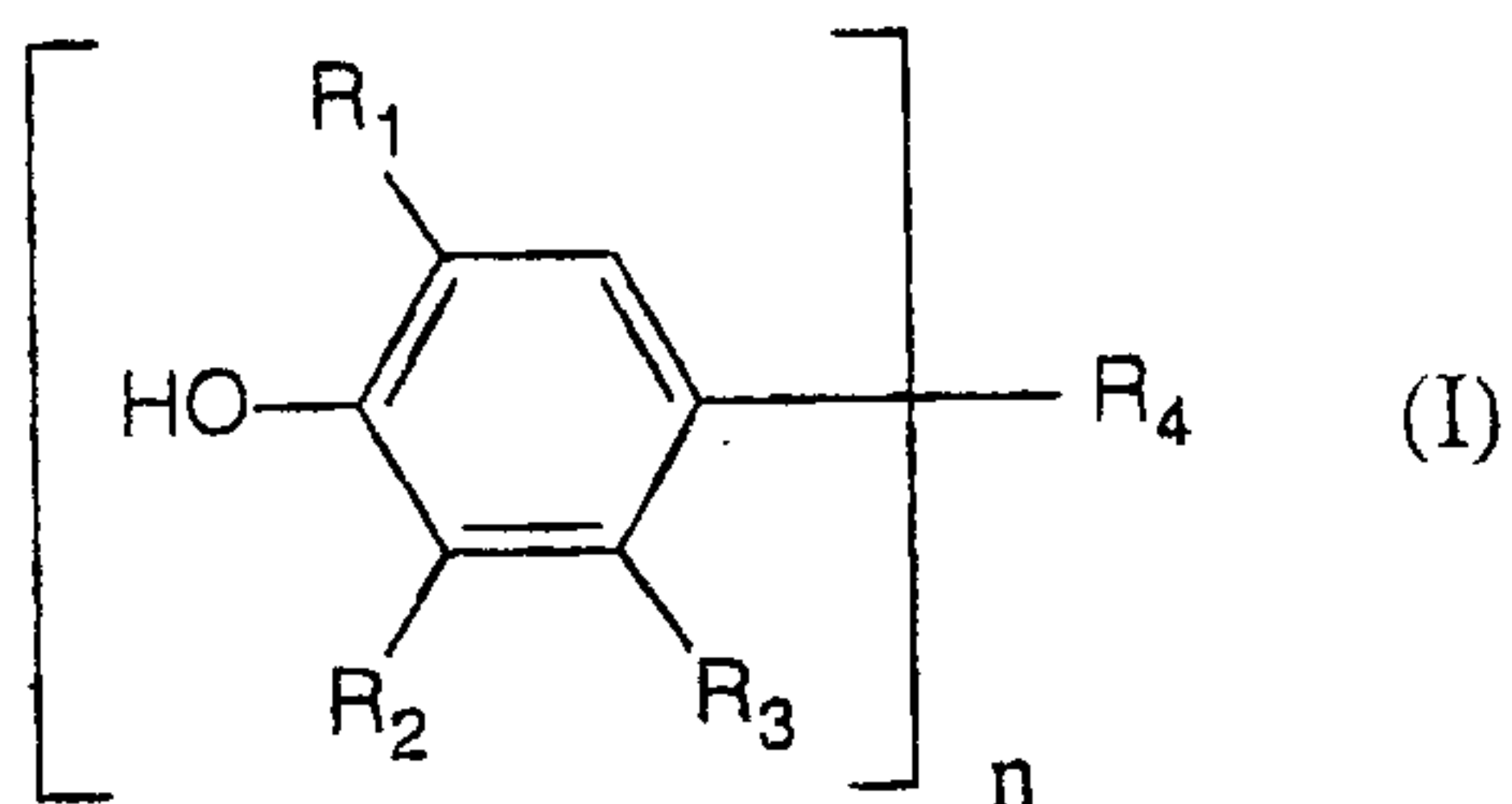
component (b) is tris(2,4-di-tert-butylphenyl) phosphite, bis(2,4-di-tert-butyl-6-methyl) ethyl phosphite or a compound of the formula Ph-3 or Ph-11



component (c) is a compound of the formula I

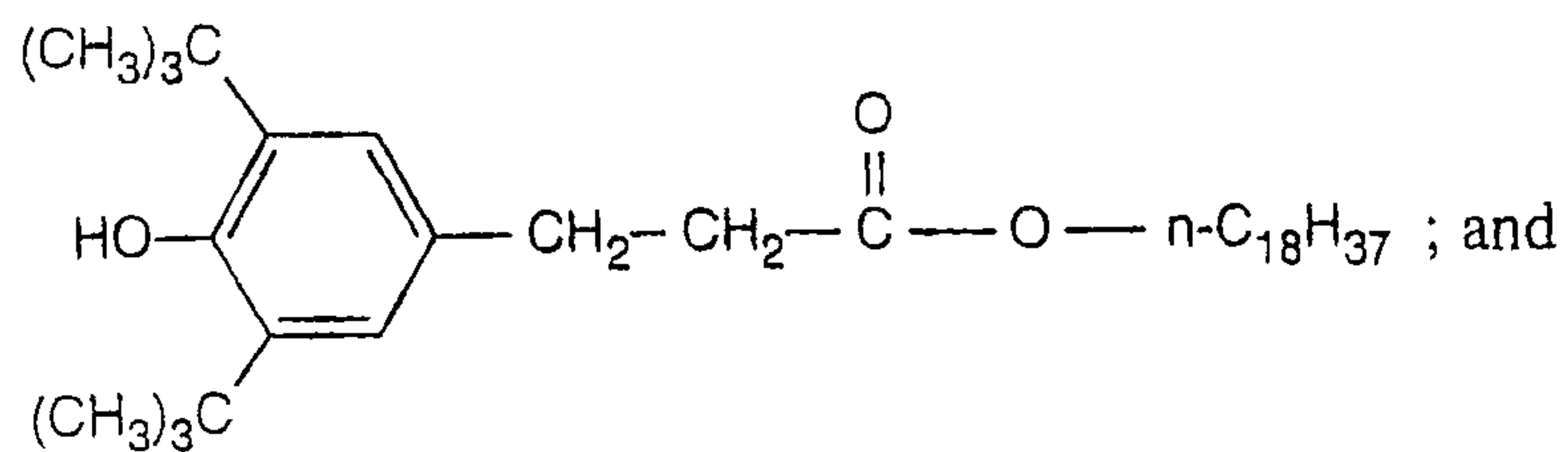
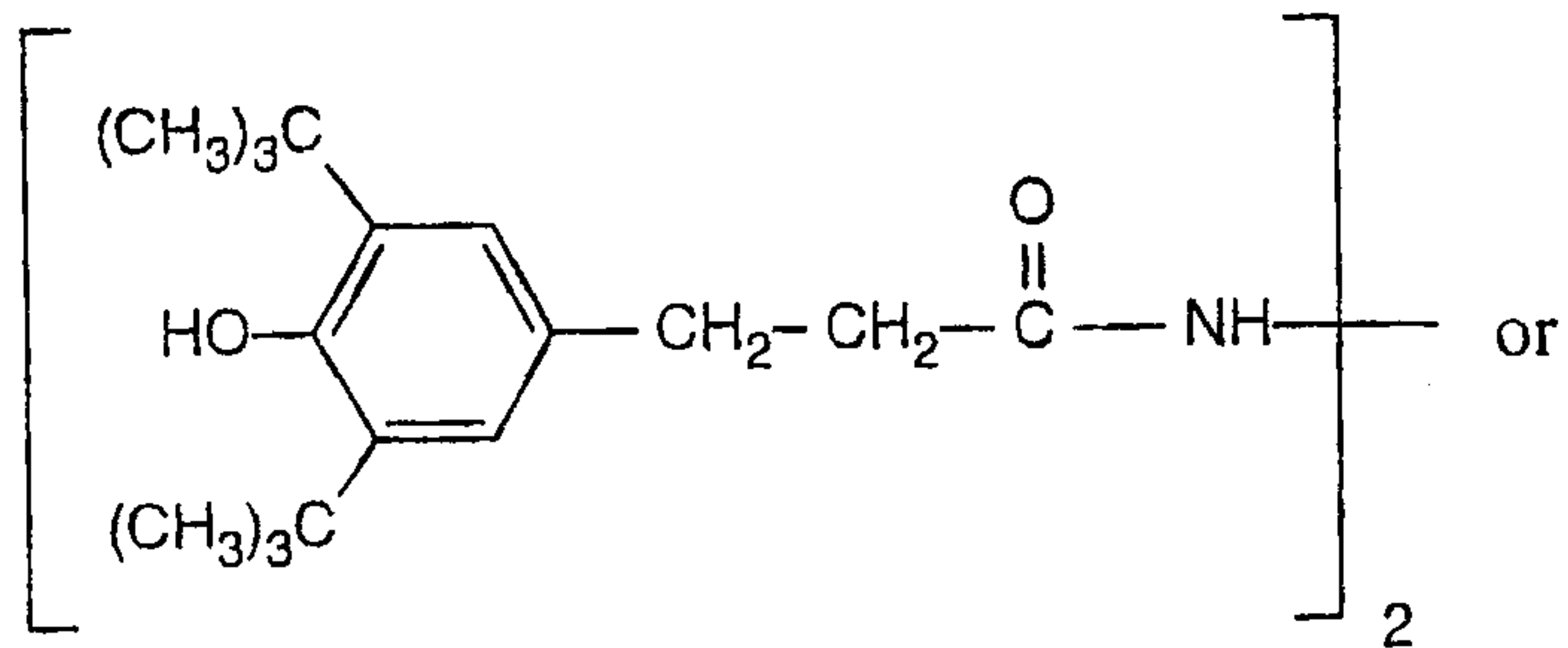
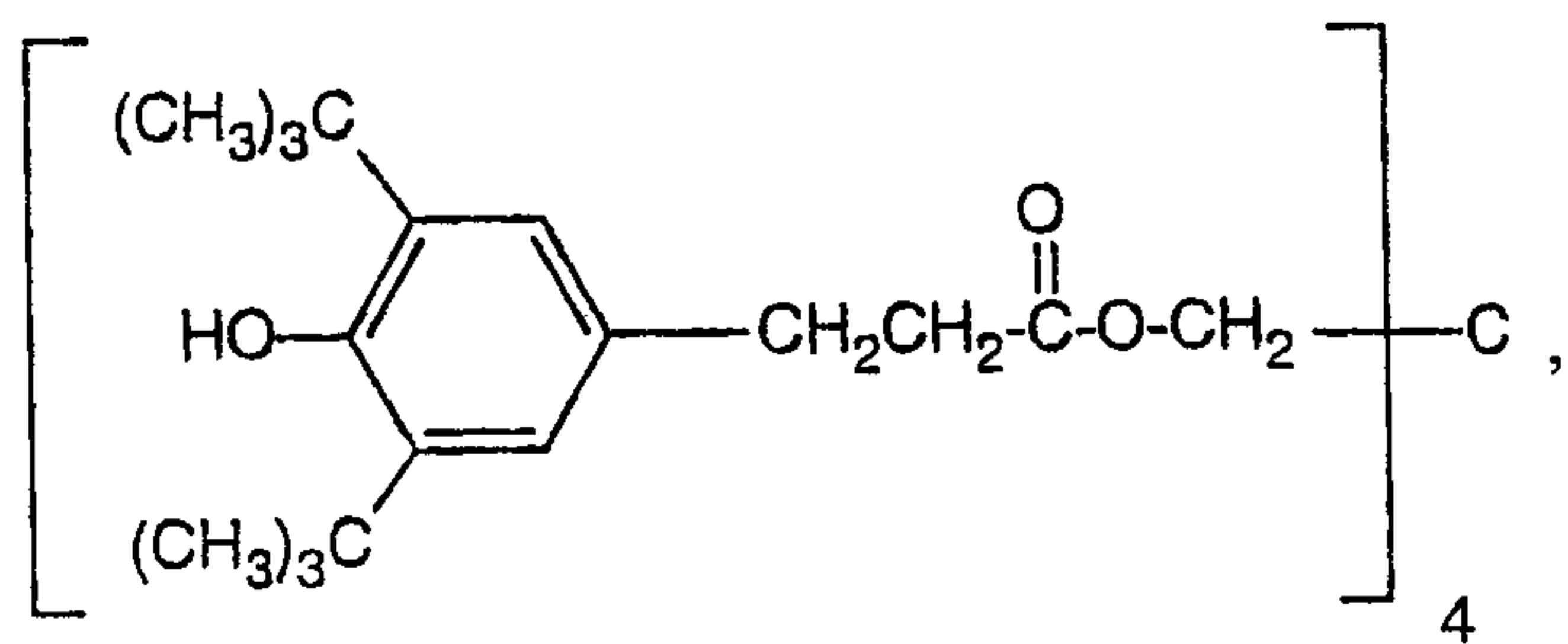
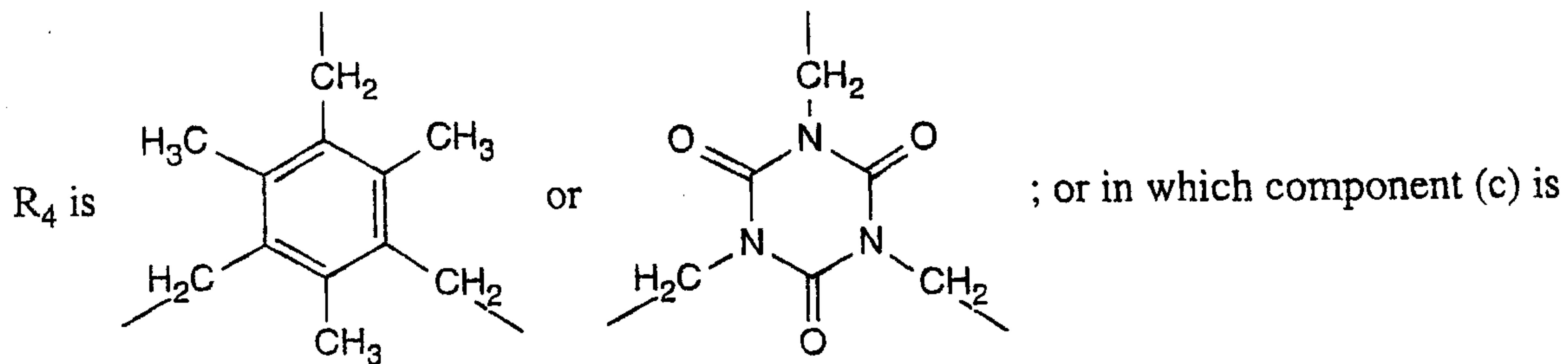
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in which

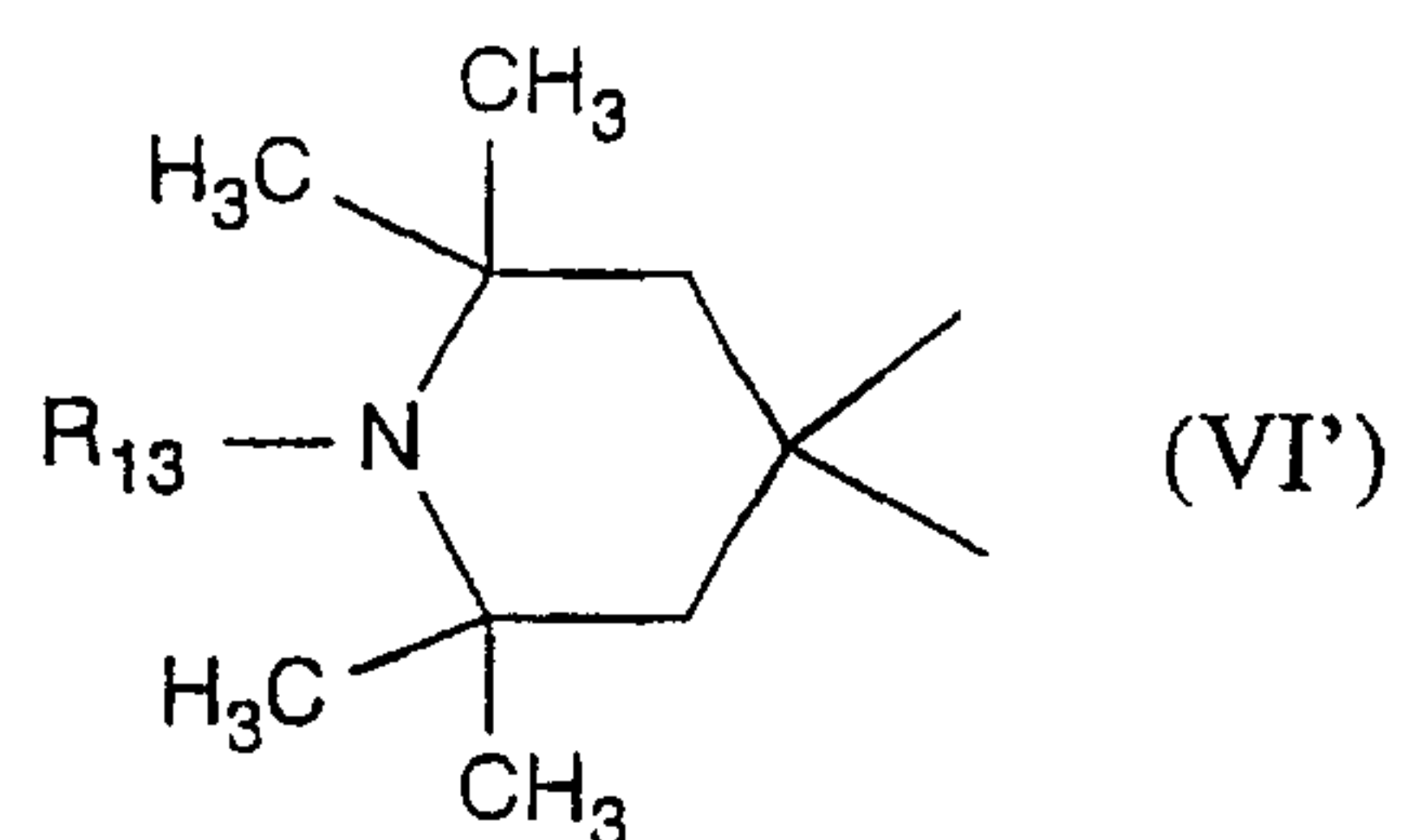
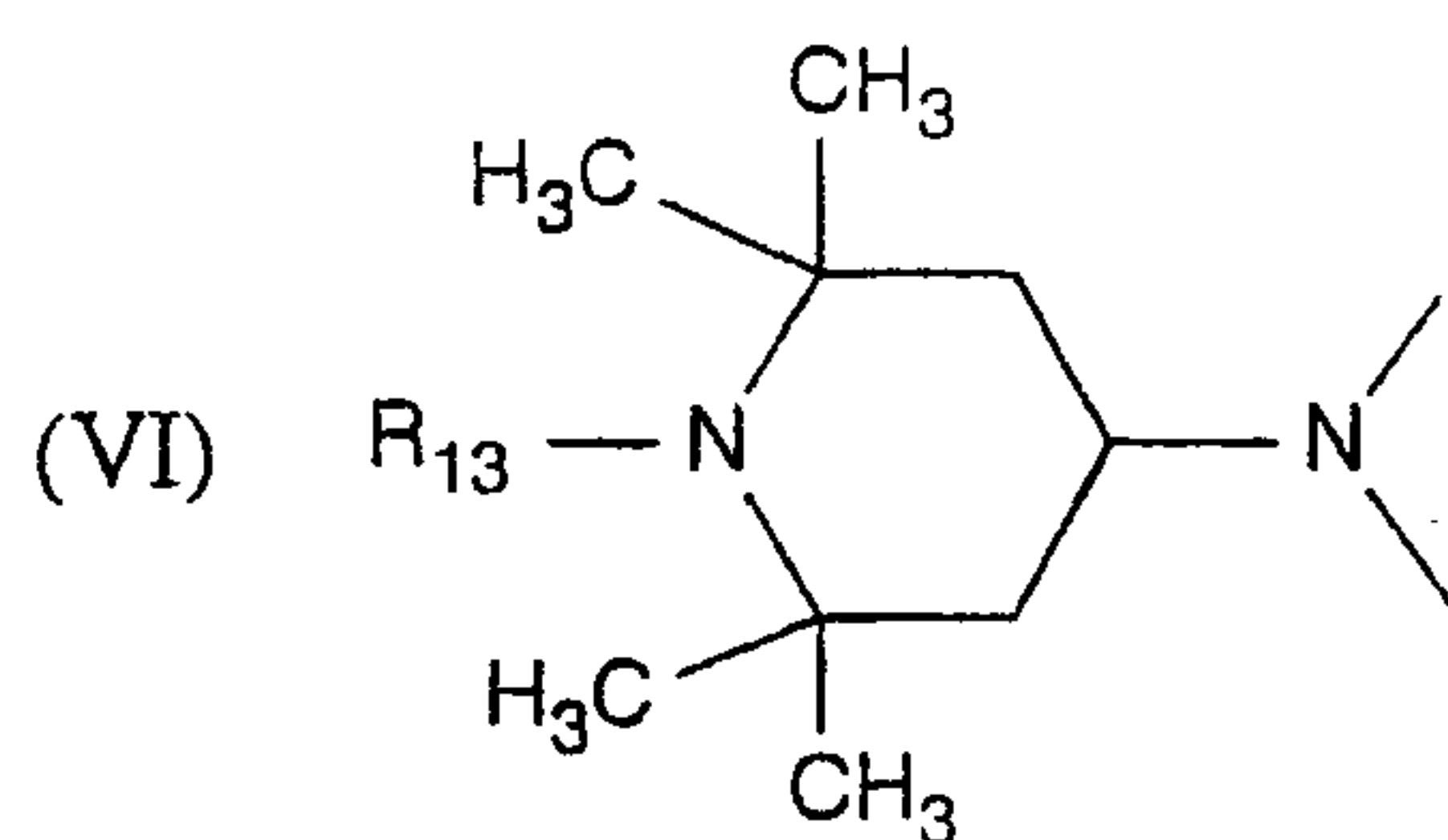
n is 3,

 R_1 and R_2 are tert-butyl, R_3 is hydrogen, and

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component (d) is a compound from the group consisting of sterically hindered amines in which the molecular weight is greater than 1000 and the compound contains at least one radical of the formula VI or VI'



in which

R_{13} is hydrogen or methyl.

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2. A process according to claim 1, wherein the mixture of components (b), (c) and (d) comprises further additives.

3. A process according to claim 1 or 2, wherein the
5 polyolefin is polyethylene or polypropylene or a copolymer thereof with a monoolefin or diolefin.

4. A process according to any one of claims 1 to 3, in which the polyolefin moulding has a wall thickness of from 1 to 50 mm.

10 5. A process according to any one of claims 1 to 4, in which the polyolefin moulding is a pipe or geomembrane.

FETHERSTONHAUGH & CO.

OTTAWA, CANADA

PATENT AGENTS