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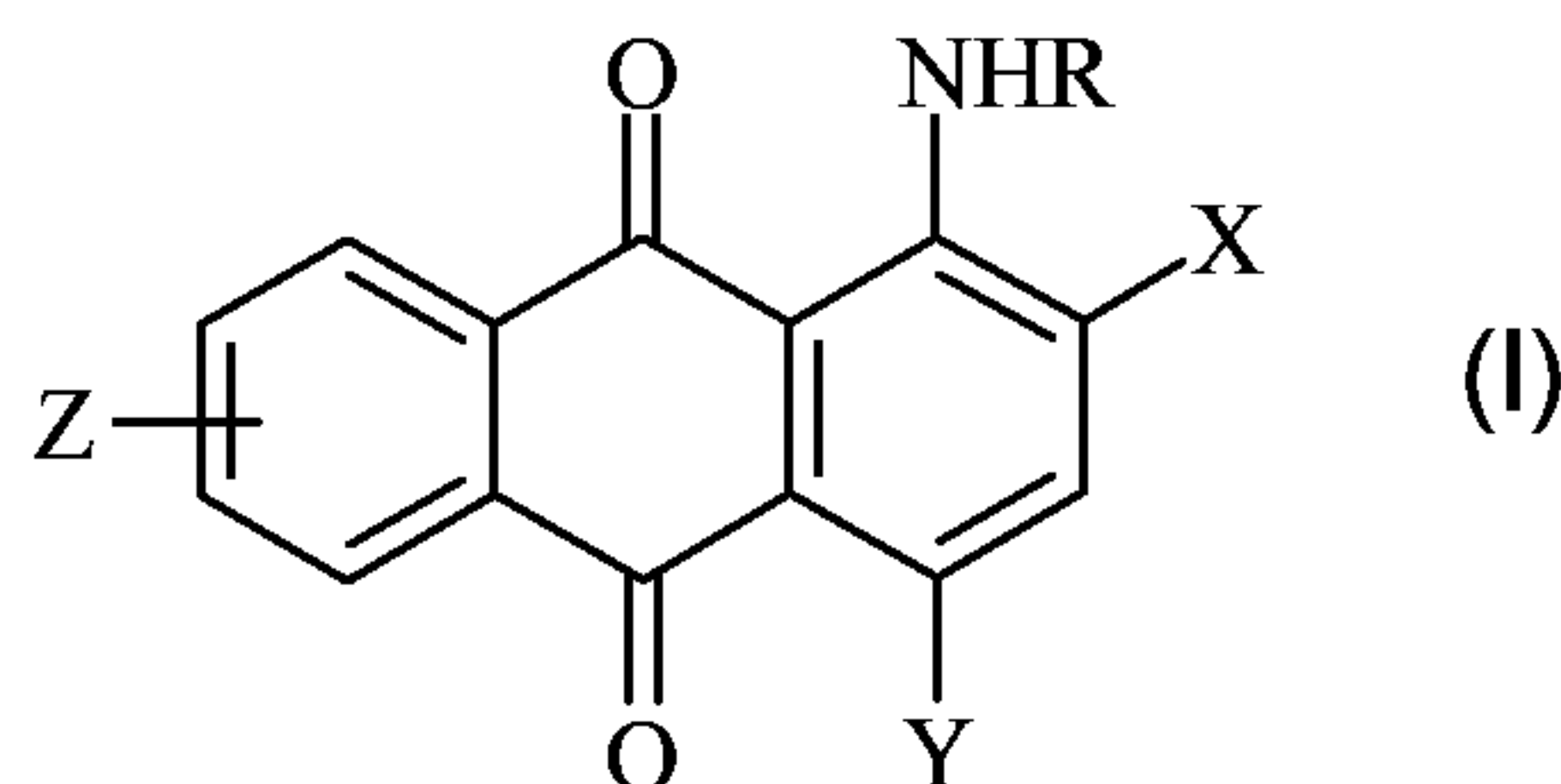
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(54) Titre : COMPOSITIONS DE COLORATION CAPILLAIRE
(54) Title: HAIR DYE COMPOSITIONS



(57) **Abrégé/Abstract:**

The present invention refers to hair dye compositions comprising one or more dyestuffs of the general formula (I) wherein R, X, Y and Z are defined as given in claim 1 and a process for colouring hair.



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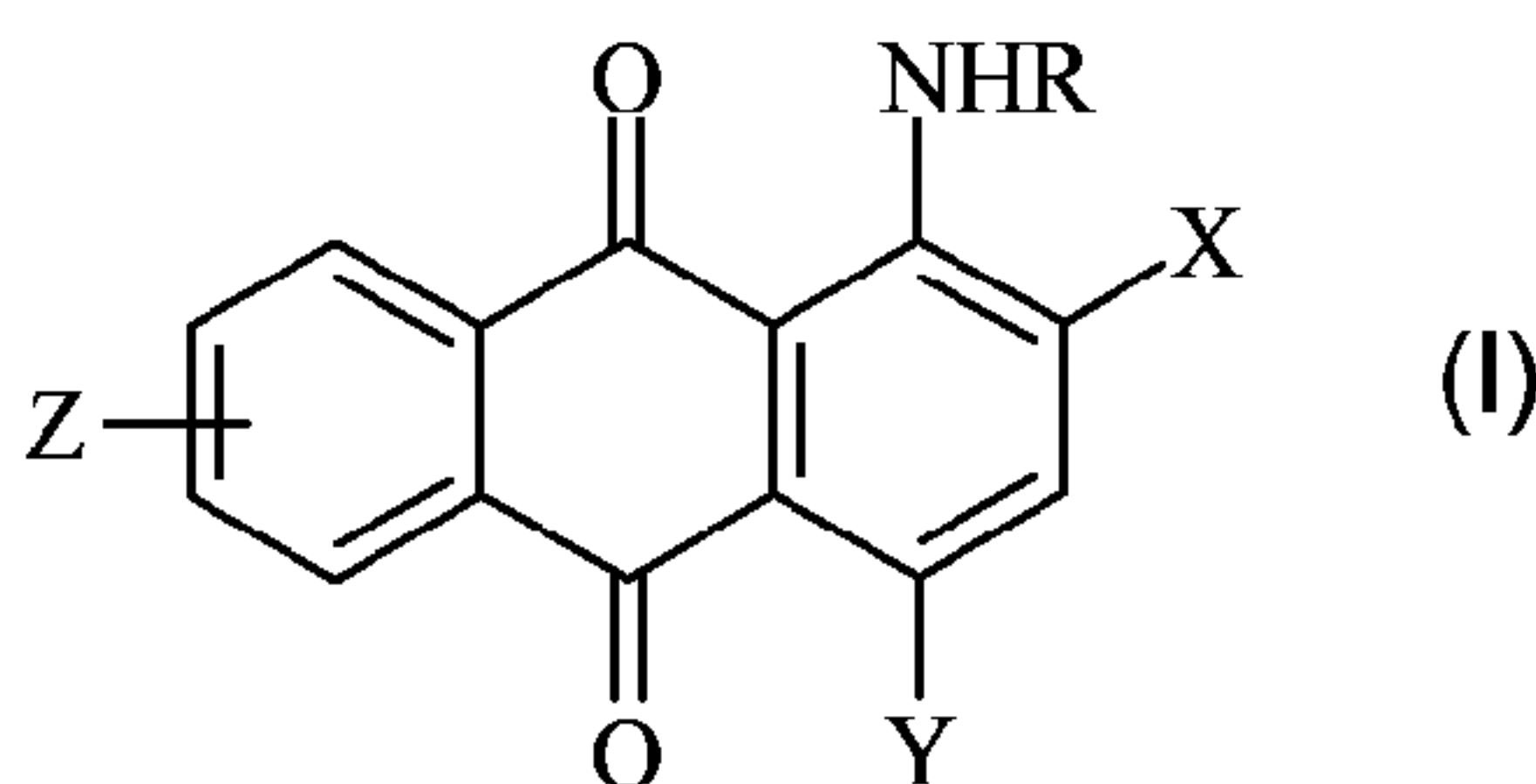
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(54) Title: HAIR DYE COMPOSITIONS



(I)

(57) **Abstract:** The present invention refers to hair dye compositions comprising one or more dyestuffs of the general formula (I) wherein R, X, Y and Z are defined as given in claim 1 and a process for colouring hair.

Hair Dye Compositions

- 5 The present invention relates to hair dye compositions containing anthraquinone hair dyes.

Hair dyes can be classified by the dye to be used therefore, or by whether they have bleaching action of melanin or not. Typical examples include a two-part permanent
10 hair dye composed of a first part containing an alkali agent, an oxidation dye and optionally a direct dye such as a nitro dye and a second part containing an oxidizing agent; and a one-part semi-permanent hair dye containing an organic acid or an alkali agent, and an acid dye, basic dye or direct dye such as a nitro dye.

The above-described permanent hair dye is however accompanied by the drawback
15 that the color tone imparted by an oxidation dye is not so vivid and that they damage the hair. Use of a nitro dye or cationic dye for a two-component hair dye containing an oxidizing agent has been attempted in order to produce various color tones (refer to, for example, Japanese Patent Laid-Open No. 1994-271435 and EP 1 133 976 A2). A permanent hair dye formulation containing current direct dyes typically
20 develop a vivid color just after dyeing, but the color fades away quickly over time and which leads to a dull end result. Also the use of many direct dyes involves such problems as decomposition when mixed with a peroxide serving as an oxidizing agent and incompatibility with the formulation.

The above described semi-permanent hair dye formulations are accompanied by the
25 drawback that the color imparted typically displays low durability. In addition, it is difficult to achieve violet, blue and ash tones since the number of dyes which can deliver these tones is extremely limited. Such dyes must be high performing and toxicologically safe.

- 30 It is known to use quaternized anthraquinone dyes to dye hairs, see for example DE 1 203 915, DE 1 248 865, DE 1 492 066, GB 1 205 365, US 3,531,502, EP 0 818 193 A2 and EP 0 852 136 A1. In addition, US 3,657,213, GB 1,270,107, GB 1,248,652, US, 2,888,467, US 2,737,517, US 4,246,172, CH 14851/71, DE 16 19

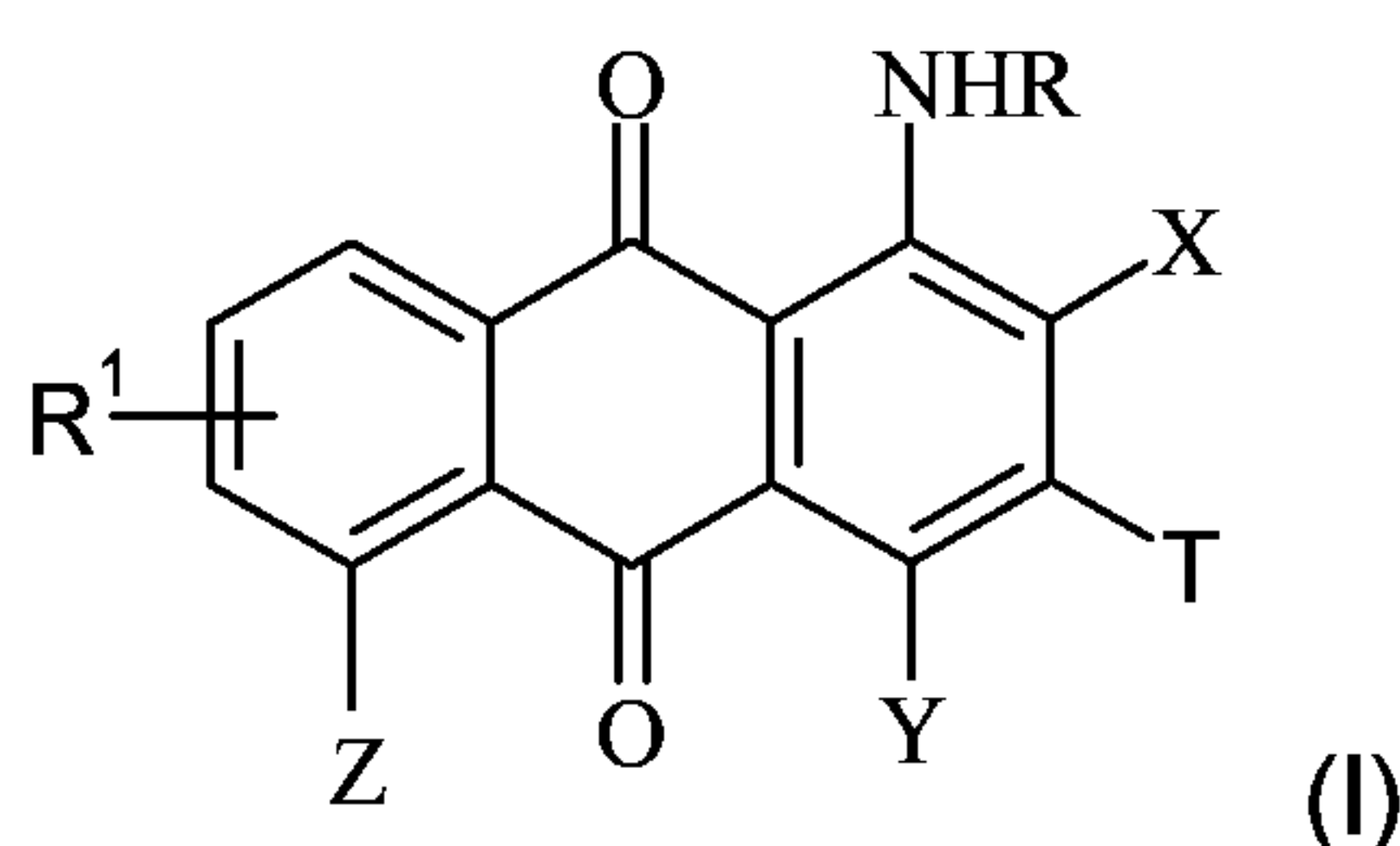
365, CH 463666, FR 1,363,216, US 5,486,629 and GB 807 241 teach to dye textile materials with quaternized anthraquinone dyes.

However, there is still a need for hair dyes which can effectively deliver blue, ash, violet or red tones to the hair without damaging and are toxicologically safe.

5

It was now surprisingly found that specific anthraquinone dyes according to the definition given below provide the required properties.

Accordingly, the present invention provides hair dye compositions comprising one or
10 more dyestuffs of the general formula (I)



wherein

R is hydrogen, alkyl, alkyl substituted by $-OR^2$, $-SR^3$ or $-NR^5R^4$, hydroxyalkyl, polyhydroxyalkyl, cycloalkyl, aryl substituted by R^{10} , $R^{11}O$ -alkyl, $-OR^{12}$, $-SR^{13}$,
15 $-NR^{14}R^{15}$, $-CONR^{15}R^{16}$, $-C(O)OR^{17}$, $-SO_2-NR^{18}R^{19}$, $-SO_2OR^{20}$, $-C(O)R^{21}$ or $-SO_2R^{22}$, $-C(O)R^6$, $-SO_2NR^7R^8$ or $-SO_2R^9$;

X is hydrogen, $-OR^{230}$, $-SR^{240}$, $-NR^{250}R^{260}$, $-SO_2NR^{270}R^{280}$, $-CONR^{290}R^{300}$,
20 $-SO_2OR^{310}$, $-C(O)OR^{320}$, $-C(O)R^{330}$, $-SO_2R^{340}$, alkyl substituted by Q, $-OR^{201}$, $-SR^{300}$ or $-NR^{500}R^{400}$, aryl substituted by R^{100} , $R^{110}O$ -alkyl, $-OR^{120}$, $-SR^{130}$, $-NR^{140}R^{150}$, $-CONR^{150}R^{160}$, $-C(O)OR^{170}$, $-SO_2-NR^{180}R^{190}$, $-SO_2OR^{200}$, $-C(O)R^{210}$ or $-SO_2R^{220}$, $-NHSO_2R^{360}R^{370}$ or $-CH=NR^{350}$;

T is hydrogen, alkyl substituted by Q or aryl substituted by $-OR^{230}$;

25

Y is hydrogen, $-NR^{51}R^{52}$, $-OR^{53}$, $-SR^{54}$, $-SO_2NHR^{55}$, $-NHC(O)R^{56}$, $-SO_2OR^{57}$, $-NHSO_2R^{58}$, $-SO_2R^{59}$, $-NHSO_2NR^{60}R^{61}$, halogen or NO_2 ;

Z is hydrogen, $-NR^{51}R^{52}$, $-OR^{53}$, $-SR^{54}$, $-SO_2NHR^{55}$, $-NHC(O)R^{56}$, $-SO_2OR^{57}$,
30 $-NHSO_2R^{58}$, $-SO_2R^{59}$, $-NHSO_2NR^{60}R^{61}$, halogen or NO_2 ;

R^1 is hydrogen, -OH, -NH₂, -NHalkyl or NO₂;

each of R^2 to R^8 , R^{60} and R^{61} , independently, is hydrogen, alkyl, aryl, hydroxyalkyl,
5 polyhydroxyalkyl or cycloalkyl;

R^9 is alkyl, aryl, hydroxyalkyl, polyhydroxyalkyl or cycloalkyl;

each of R^{10} to R^{21} , independently, is hydrogen, alkyl, hydroxyalkyl, polyhydroxyalkyl
10 or cycloalkyl;

R^{22} is alkyl, hydroxyalkyl, polyhydroxyalkyl or cycloalkyl;

each of R^{51} to R^{54} , independently, is hydrogen, alkyl, hydroxyalkyl, polyhydroxyalkyl,
15 cycloalkyl, cycloalkyl substituted by -C(O) R^6 , -SO₂ R^9 , or aryl substituted by R^{10} ,
 R^{11} O-alkyl, -OR¹², -SR¹³, -NR¹⁴ R^{15} , -CONR¹⁵ R^{16} , -C(O)OR¹⁷,
-SO₂-NR¹⁸ R^{19} , -SO₂OR²⁰, -C(O) R^{21} or -SO₂ R^{22} ;

each of R^{55} to R^{57} , independently, is hydrogen, alkyl, hydroxyalkyl, polyhydroxyalkyl,
20 cycloalkyl or aryl substituted by R^{10} , R^{11} O-alkyl, -OR¹², -SR¹³, -NR¹⁴ R^{15} , -CONR¹⁵ R^{16} ,
-C(O)OR¹⁷, -SO₂-NR¹⁸ R^{19} , -SO₂OR²⁰, -C(O) R^{21} or -SO₂ R^{22} ;

each R^{58} and R^{59} , independently, is alkyl, hydroxyalkyl, polyhydroxyalkyl, cycloalkyl
or aryl substituted by R^{10} , R^{11} O-alkyl, -OR¹², -SR¹³, -NR¹⁴ R^{15} , -CONR¹⁵ R^{16} , -
25 C(O)OR¹⁷, -SO₂-NR¹⁸ R^{19} , -SO₂OR²⁰, -C(O) R^{21} or -SO₂ R^{22} ;

each of R^{230} , R^{240} and R^{350} , independently, is alkyl substituted by Q, hydroxyalkyl
substituted in the alkyl group by Q, polyhydroxyalkyl substituted in the alkyl group by
Q, cycloalkyl substituted by Q, -C(O) R^{600} or -SO₂ R^{900} , or aryl substituted by R^{100} ,
30 R^{110} O-alkyl, -OR¹²⁰, -SR¹³⁰, -NR¹⁴⁰ R^{150} , -CONR¹⁵⁰ R^{160} , -C(O)OR¹⁷⁰,
-SO₂-NR¹⁸⁰ R^{190} , -SO₂OR²⁰⁰, -C(O) R^{210} or -SO₂ R^{220} ;

each of R^{201} , R^{200} , R^{600} , R^{900} , independently, is alkyl substituted by Q, aryl substituted by Q, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl substituted by Q,

- 5 each of R^{100} , R^{110} , R^{120} , R^{130} , R^{170} , R^{200} , R^{210} , R^{220} , independently, is alkyl substituted by Q, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl substituted by Q,

- each of R^{140} , R^{150} , R^{160} , R^{180} and R^{190} is hydrogen, alkyl, alkyl substituted by Q,
 10 hydroxyalkyl, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl or cycloalkyl substituted by Q, with the proviso that each the groups $-NR^{140}R^{150}$, $-CONR^{150}R^{160}$ and $-SO_2-NR^{180}R^{190}$ must contain one group Q;

- 15 each of R^{310} , R^{320} , R^{330} and R^{340} , independently, is alkyl substituted by Q, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl substituted by Q or aryl substituted by R^{100} , R^{110} O-alkyl, - OR^{120} , $-SR^{130}$, $-NR^{140}R^{150}$, $-CONR^{150}R^{160}$, $-C(O)OR^{170}$, $-SO_2-NR^{180}R^{190}$, $-SO_2OR^{200}$, $-C(O)R^{210}$ or $-SO_2R^{220}$;

- 20 each of R^{360} and R^{370} is hydrogen, alkyl, alkyl substituted by Q, aryl, aryl substituted by Q, hydroxyalkyl, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl or cycloalkyl substituted by Q, with the proviso that the group $-NHSO_2R^{360}R^{370}$ must contain one
 25 group Q;

- each of R^{250} , R^{260} , R^{270} , R^{280} , R^{290} and R^{300} , independently, is hydrogen, alkyl, alkyl substituted by Q, hydroxyalkyl, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl or
 30 cycloalkyl substituted by Q, $-C(O)R^{601}$, $-SO_2R^{901}$, or aryl substituted by R^{101} , R^{111} O-alkyl, $-OR^{121}$, $-SR^{131}$, $-NR^{141}R^{151}$, $-CONR^{151}R^{161}$, $-C(O)OR^{171}$, $-SO_2-NR^{181}R^{191}$, $-SO_2OR^{202}$, $-C(O)R^{211}$ or $-SO_2R^{221}$, with the proviso that each of the groups $-NR^{250}R^{260}$, $-SO_2NR^{270}R^{280}$ and $-CONR^{290}R^{300}$ must contain one group Q;

each of R^{111} , R^{121} , R^{131} , R^{141} , R^{151} , R^{161} , R^{171} , R^{181} , R^{191} , R^{202} and R^{211} , independently, is hydrogen, alkyl, alkyl substituted by Q, hydroxyalkyl, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl or cycloalkyl substituted by Q;

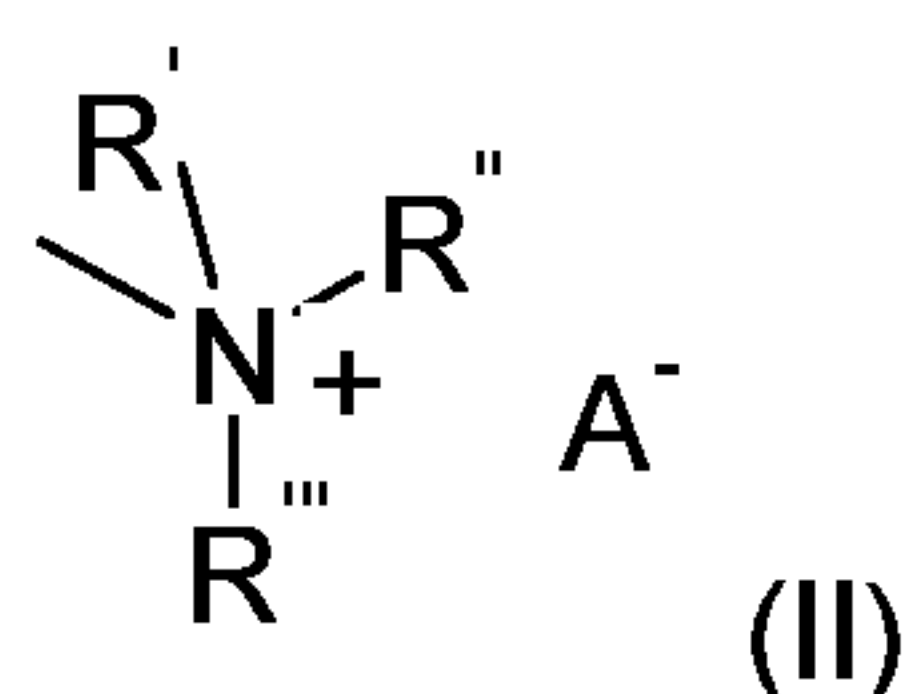
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R^{221} is alkyl, alkyl substituted by Q, hydroxyalkyl, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl or cycloalkyl substituted by Q;

10 R^{601} is hydrogen, alkyl, alkyl substituted by Q, aryl, aryl substituted by Q, hydroxyalkyl, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl or cycloalkyl substituted by Q; and

15 R^{901} is alkyl, alkyl substituted by Q, aryl, aryl substituted by Q, hydroxyalkyl, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl or cycloalkyl substituted by Q; and

Q is a group of the general formula (II)



20

wherein

each of R' , R'' and R''' , independently, is alkyl, aryl, arylalkyl, cycloalkyl, cycloalkylalkyl, heteroaryl, heteroarylalkyl, heterocycloalkyl, heterocycloalkyl-alkyl, either of which can be substituted by heteroatom containing groups or R' and R''

25 form together with the nitrogen to which they are bonded a 5- or 6- membered heterocyclic ring; and

A^- is a cosmetically acceptable anion;

whereby the dyestuff of the formula (I) contains exactly one group Q;

30 whereby at least one of the groups Y and Z are groups other than hydrogen; and whereby T and R^1 are hydrogen if X is different from hydrogen.

Alkyl groups may be straight-chain or branched and are preferably (C₁-C₆)-alkyl groups, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, n-pentyl, isopentyl or n-hexyl.

- 5 Cycloalkyl is preferably (C₃-C₈)-cycloalkyl and especially preferably cyclopentyl and cyclohexyl.

Aryl groups are preferably phenyl or naphthyl groups.

- 10 Halogen is preferably chlorine, bromine and fluorine.

A 5- or 6- membered heterocyclic ring which is formed by R' and R'' is preferably a pyrrolidine, piperidine, morpholine or piperazine ring. R', R'' and R''' are preferably benzyl or (C₁-C₆)-alkyl and especially preferably benzyl, methyl and ethyl.

15

The dyestuffs of the general formula (I) may be salts of an organic or inorganic acid. Consequently, A⁻ may be for example chloride, bromide, iodide, hydroxide, hydrogenphosphate, phosphate, carbonate, hydrogencarbonate, hydrogensulfate, perchlorate, fluoroborate, chlorozincate, methylsulfate, ethylsulfate, acetate, propionate, lactate or citrate or mixtures thereof.

20

The meaning of A⁻ is generally given by the preparation method of the dyestuff of the general formula (I). Preferred meanings of A⁻ are chloride, sulfate, hydrogensulfate, methylsulfate, ethylsulfate, phosphate, formate, acetate and lactate.

25

Especially preferred dye compositions of the present invention comprise one or more dyestuffs of the general formula (I) in which

Z, T and R¹ are hydrogen;

R is hydrogen or (C₁-C₆)-alkyl;

Y is -NR⁵¹R⁵², -NH₂SO₂R⁵⁸ or -OR⁵³, wherein R⁵¹ is hydrogen and R⁵² is hydrogen,

30

(C₁-C₆)-alkyl, hydroxy-(C₁-C₆)-alkyl or phenyl; R⁵³ is hydrogen, (C₁-C₆)-alkyl or phenyl; and R⁵⁸ is (C₁-C₆)-alkyl or phenyl;

X is -OR²³⁰ or -SR²⁴⁰, wherein R²³⁰ and R²⁴⁰ are (C₁-C₆)-alkyl substituted by Q, phenyl substituted by Q, (C₁-C₆)-alkyl-SO₂-phenyl wherein the alkyl group is

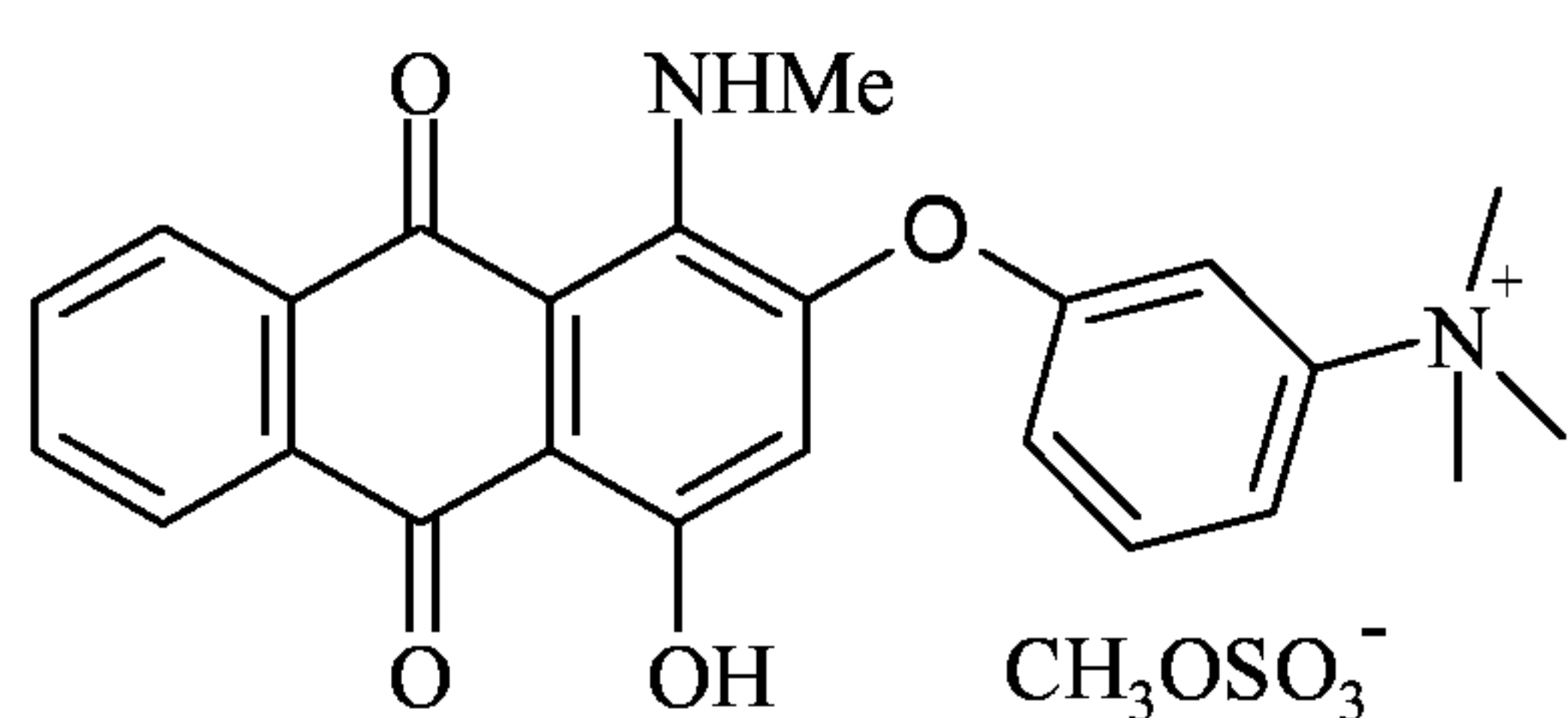
substituted by Q or (C₁-C₆)-alkyl-NH-SO₂-phenyl, wherein the alkyl group is substituted by Q;

Q is a tris-(C₁-C₆)-alkyl-ammonium group, a bis(C₁-C₆)-alkyl-benzyl-ammonium group, a methyl-morpholinium group or a methyl-pyrrolidinium group; and

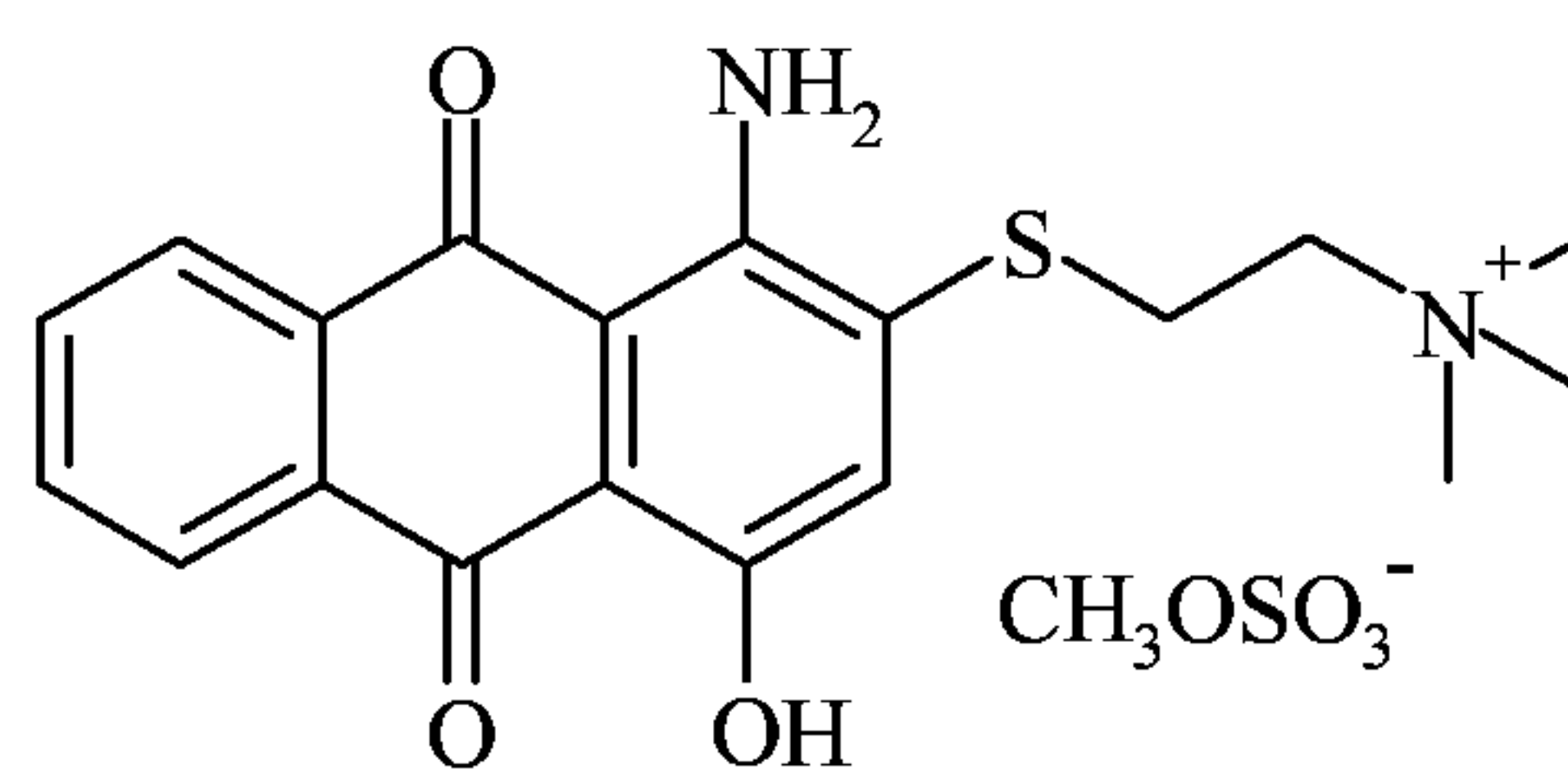
5 A⁻ is chloride, sulfate, hydrogensulfate, methylsulfate, ethylsulfate, phosphate, formate, acetate or lactate.

Examples of dyestuffs of this type are the dyestuffs of of the formulae (lc), (lg), (lh), (li), (lr), (ls), (ldd), (lee and (lff)

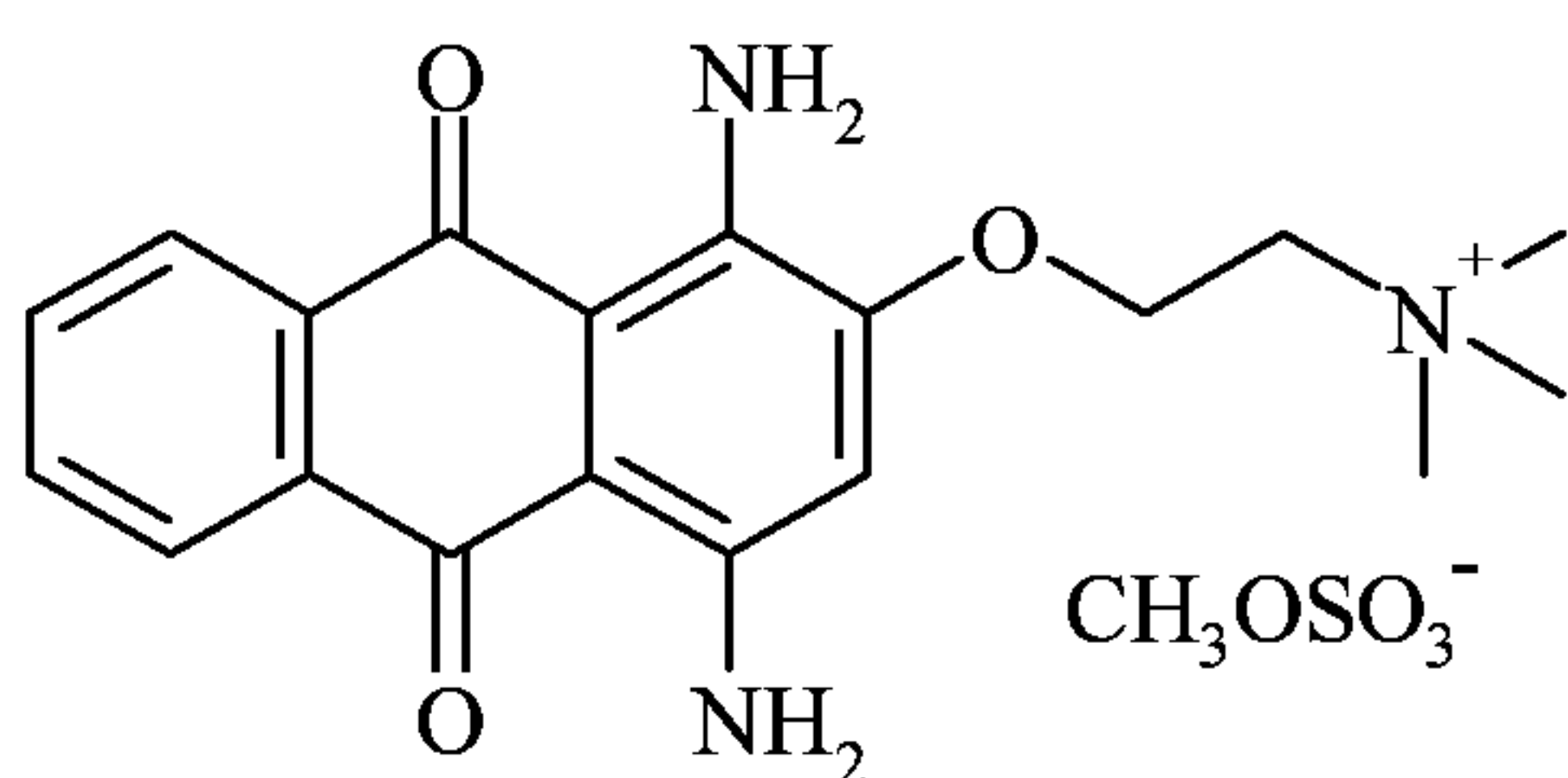
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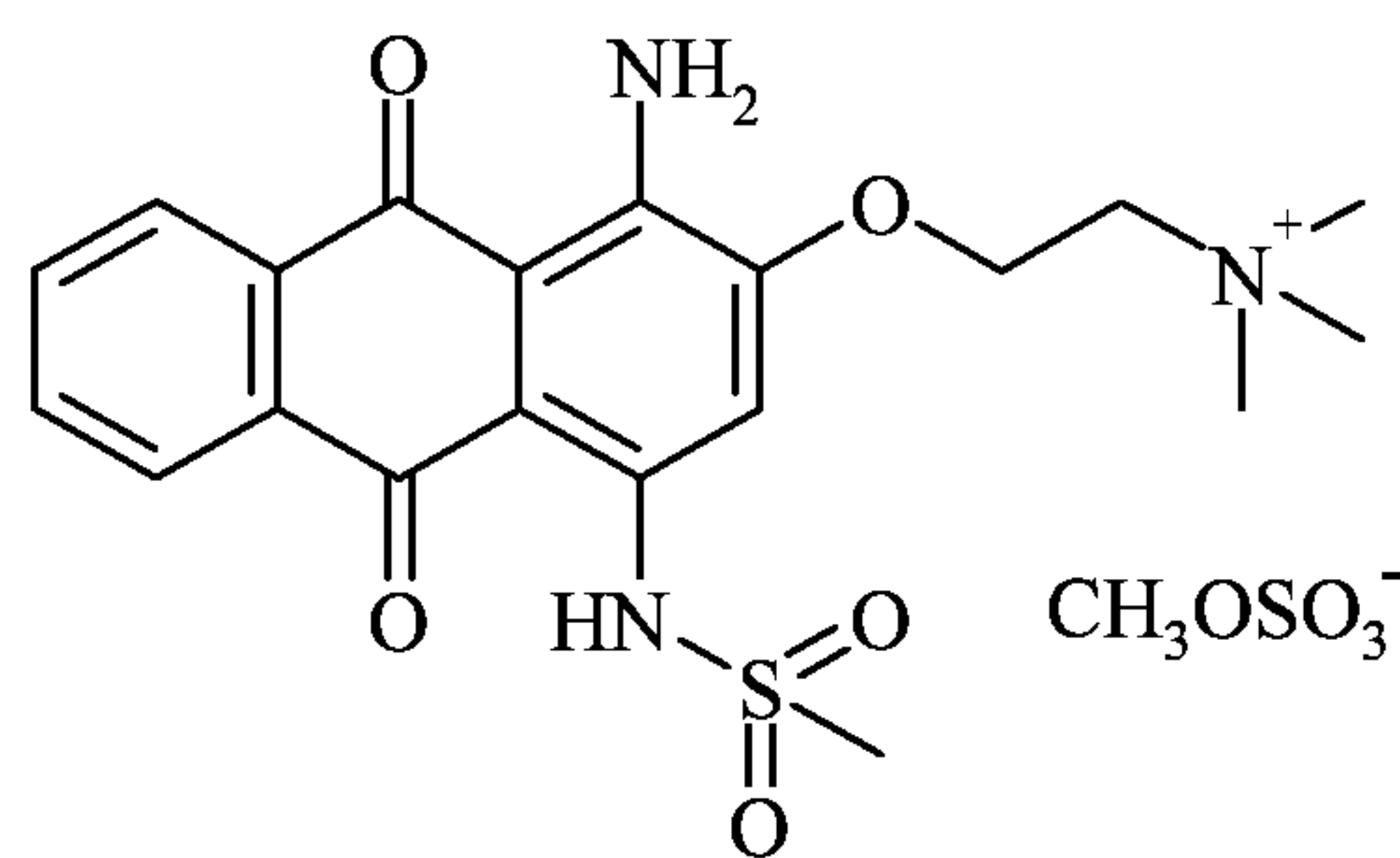
(lc)



(lg)

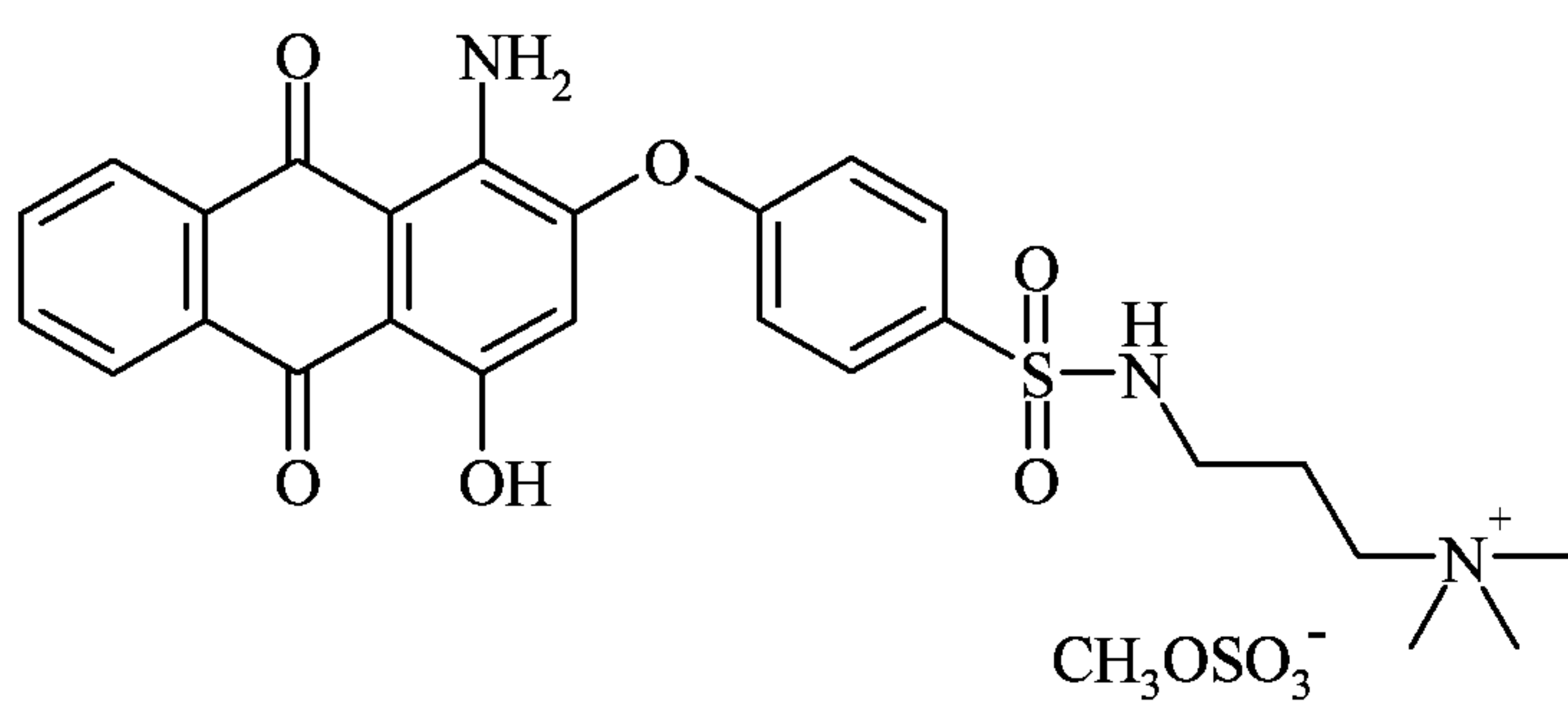


(lh)

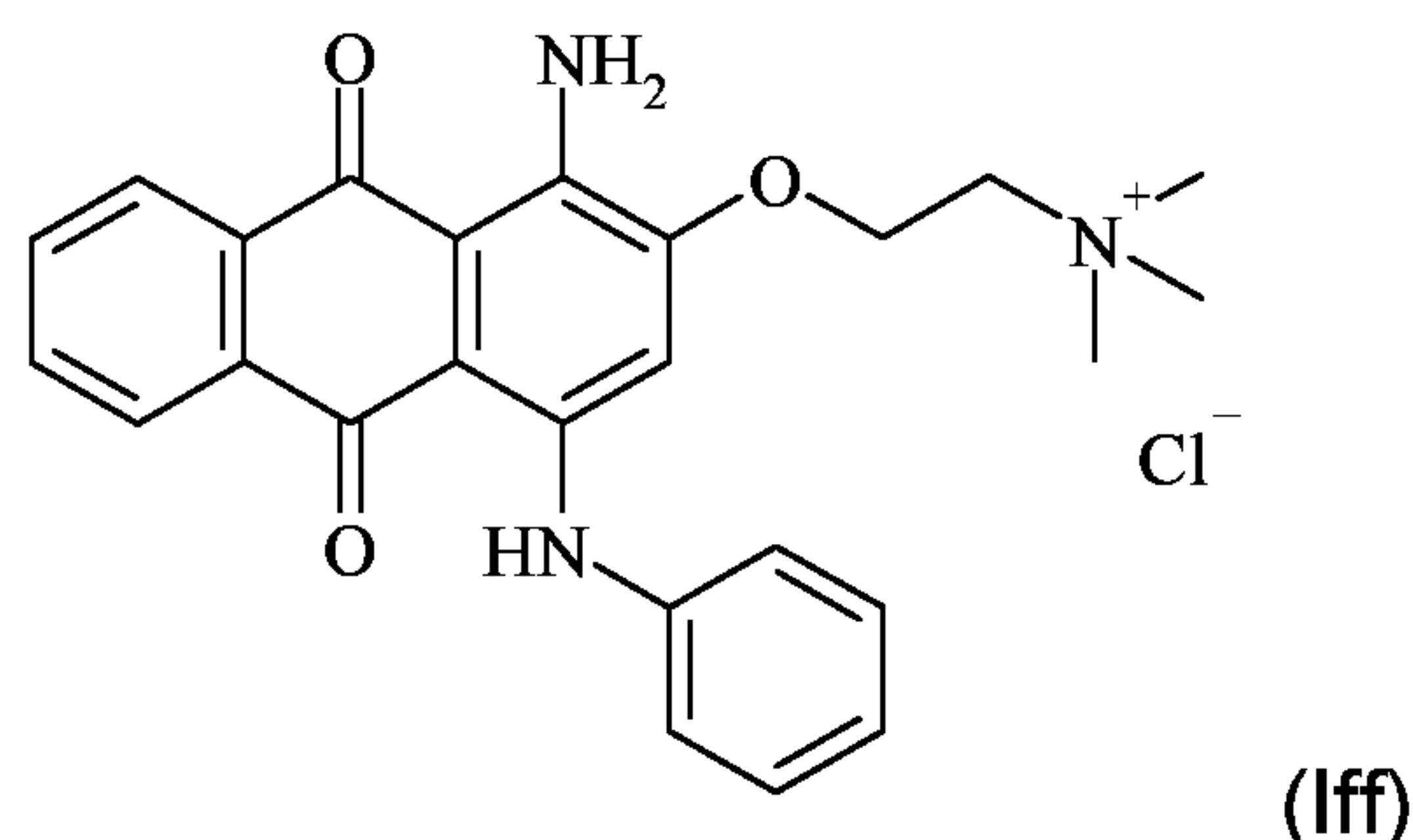
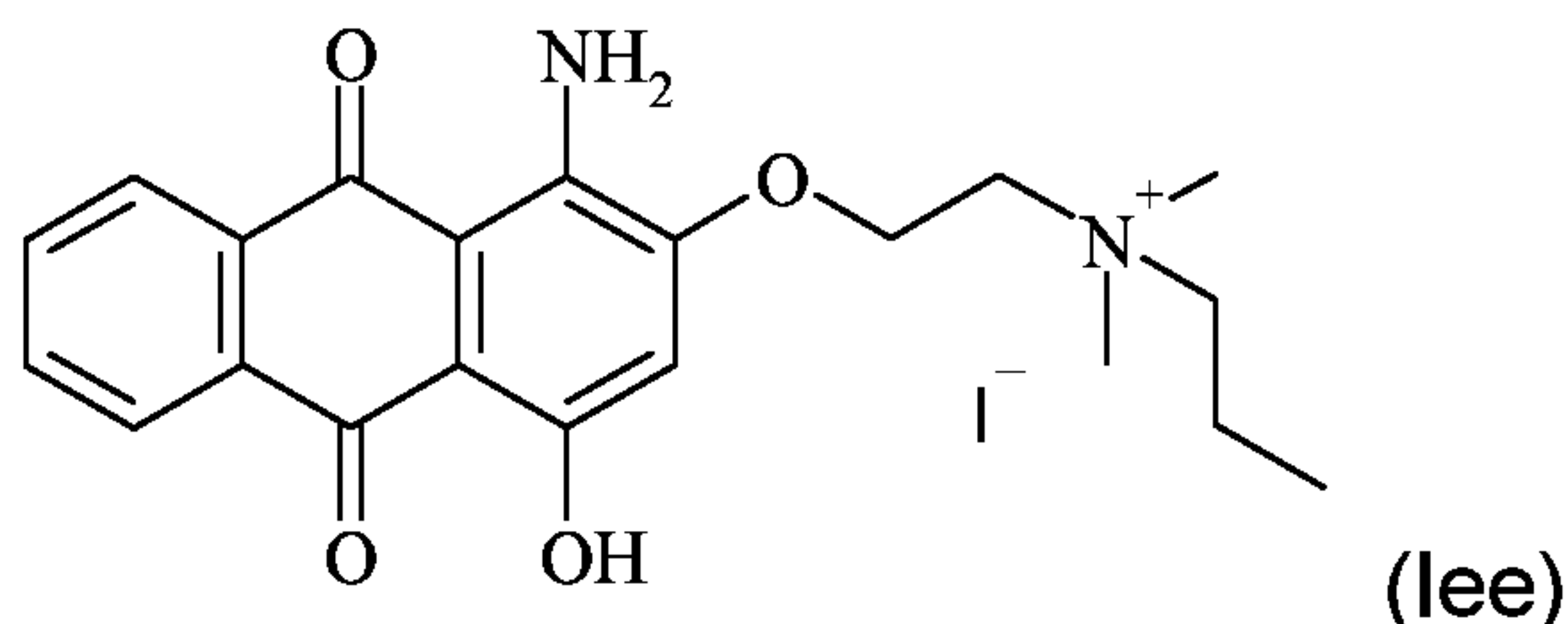
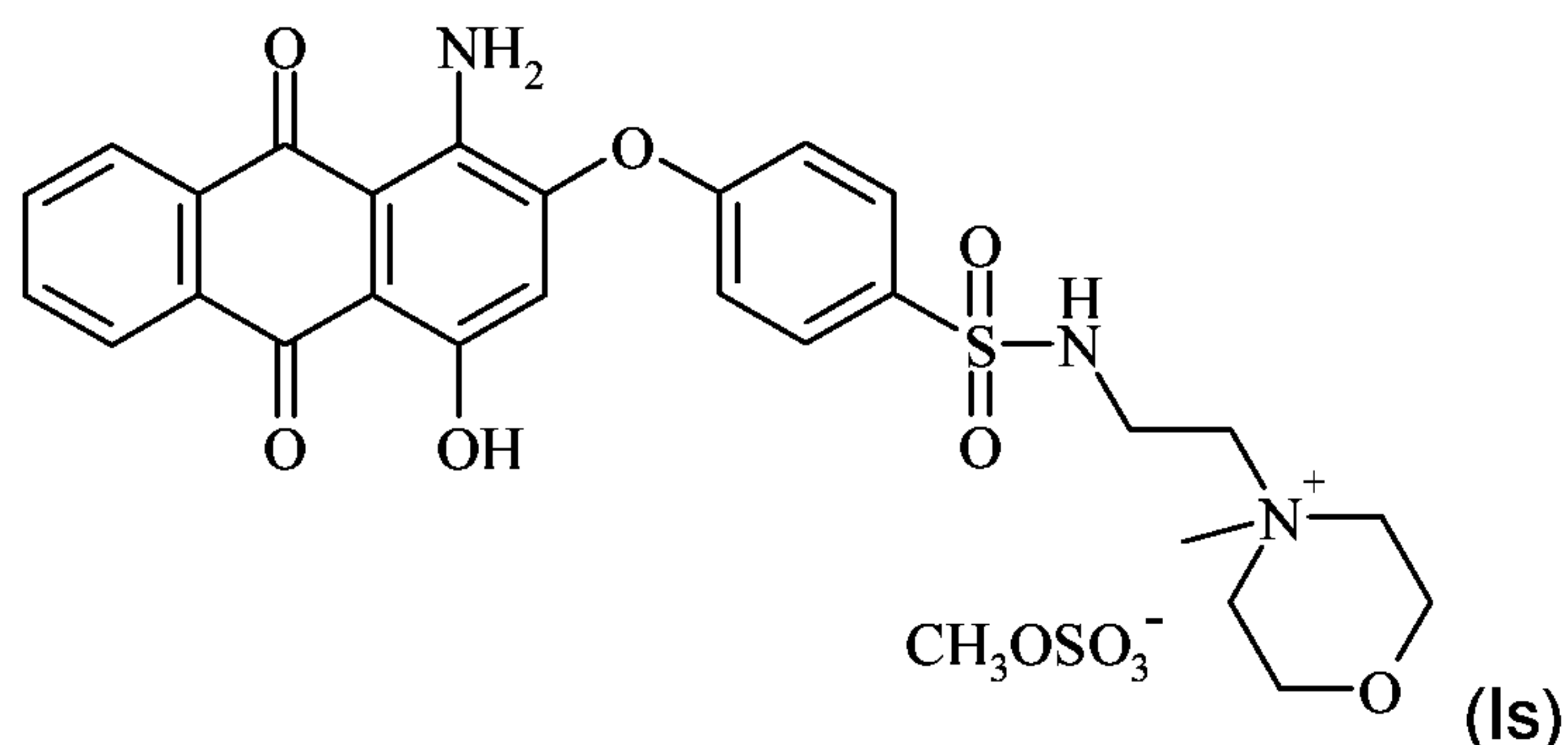
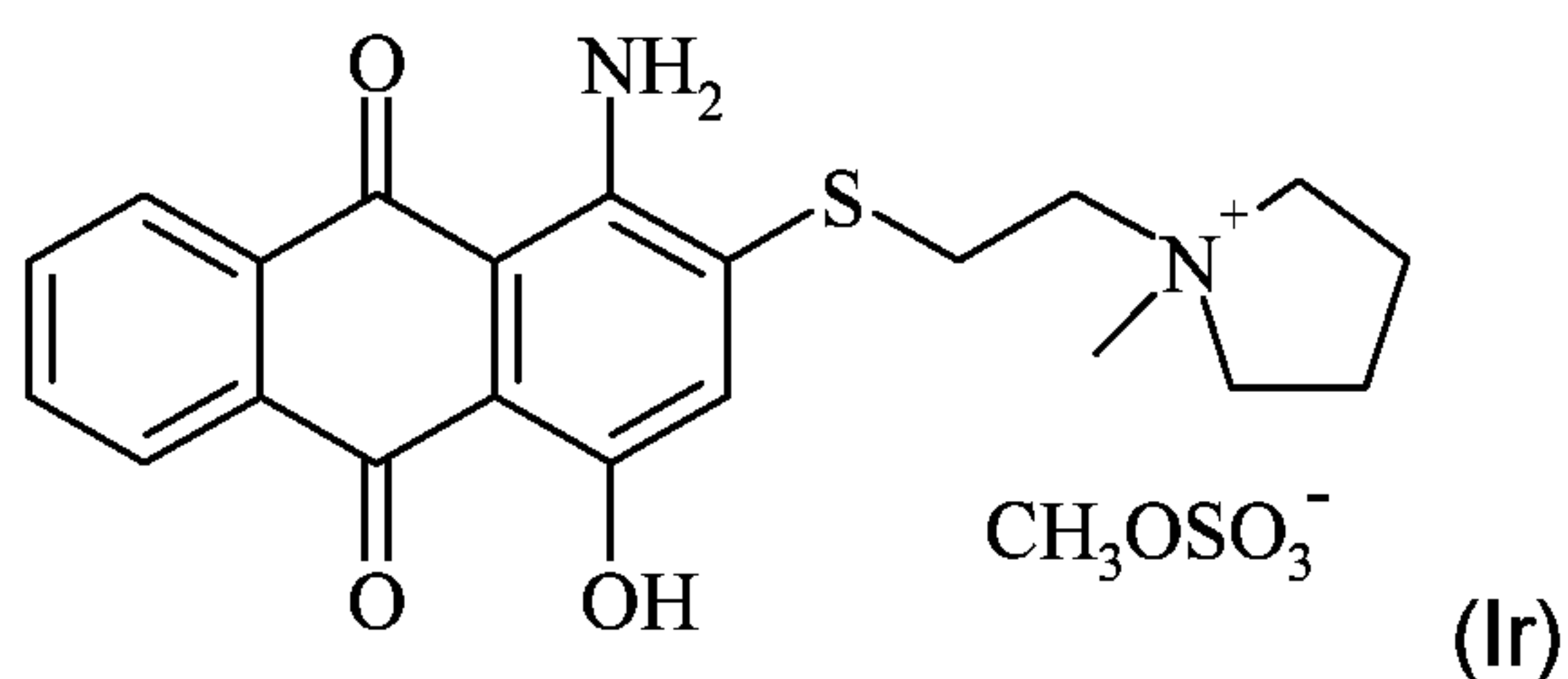


(ldd)

15



(li)



Further especially preferred dye compositions of the present invention comprise one or more dyestuffs of the general formula (I) in which

10 R is hydrogen or (C₁-C₆)-alkyl;

Z, T and R¹ are hydrogen;

Y is -NR⁵¹R⁵² or OR⁵³, wherein R⁵¹ and R⁵³ are hydrogen, R⁵² is (C₁-C₆)-alkyl, hydroxy-(C₁-C₆)-alkyl or phenyl;

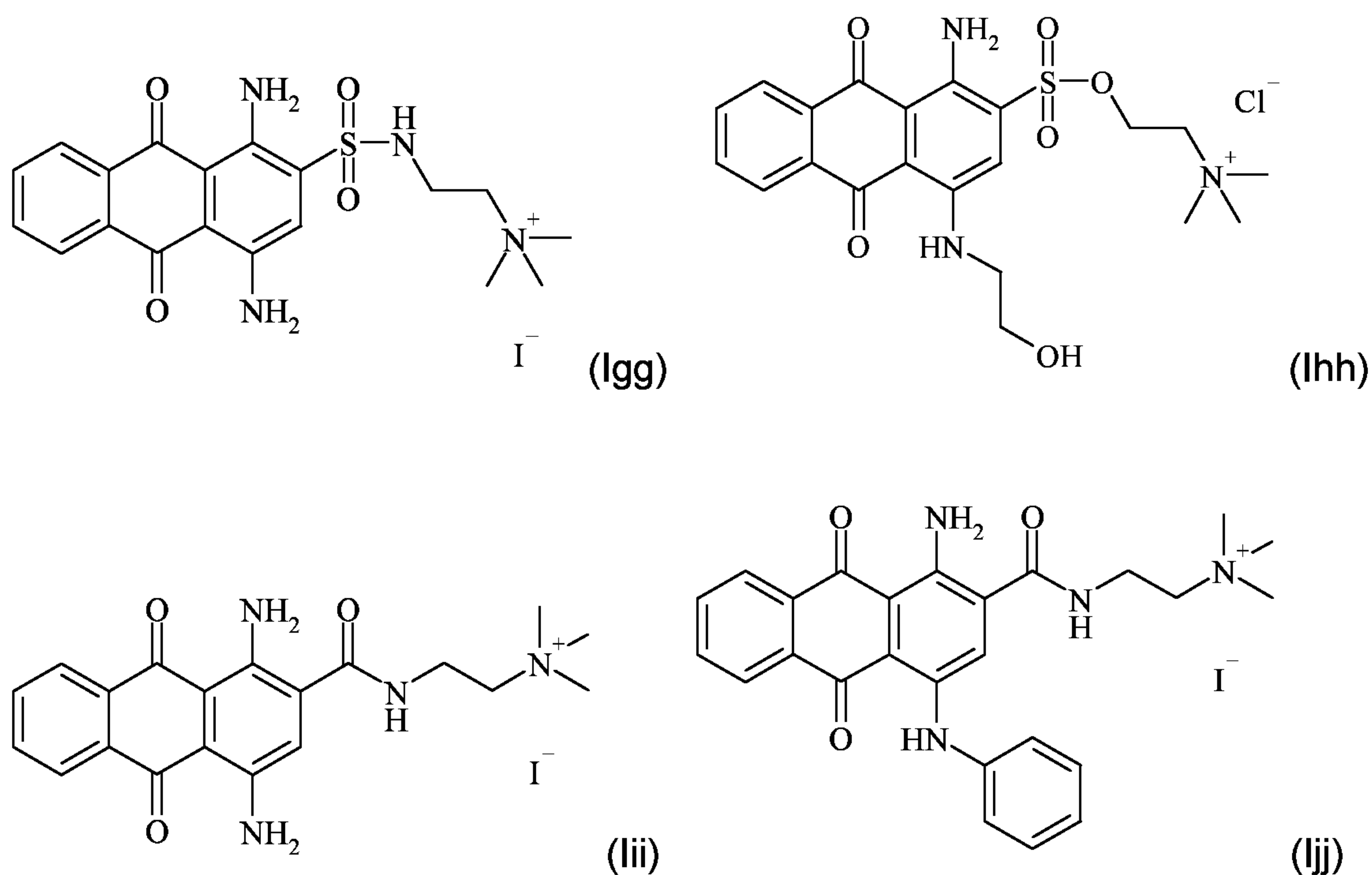
15 X is -SO₂NR²⁷⁰R²⁸⁰, -CONR²⁹⁰R³⁰⁰, -SO₂OR³¹⁰, -C(O)OR³²⁰, wherein R²⁷⁰ and R²⁹⁰ are hydrogen or (C₁-C₆)-alkyl; R²⁸⁰, R³⁰⁰, R³¹⁰ and R³²⁰ are (C₁-C₆)-alkyl substituted by Q, hydroxy(C₁-C₆)-alkyl substituted in the alkyl group by Q or phenyl substituted by Q;

Q is a tris(C₁-C₆)-alkyl-ammonium group, a bis(C₁-C₆)-alkyl-benzyl-ammonium group, a methyl-morpholinium group or a methyl-pyrrolidinium group; and

A^- is chloride, sulfate, hydrogensulfate, methylsulfate, ethylsulfate, phosphate, formate, acetate or lactate.

Examples of dyestuffs of this type are the dyestuffs of the formulae (lgg) to (ljj):

5

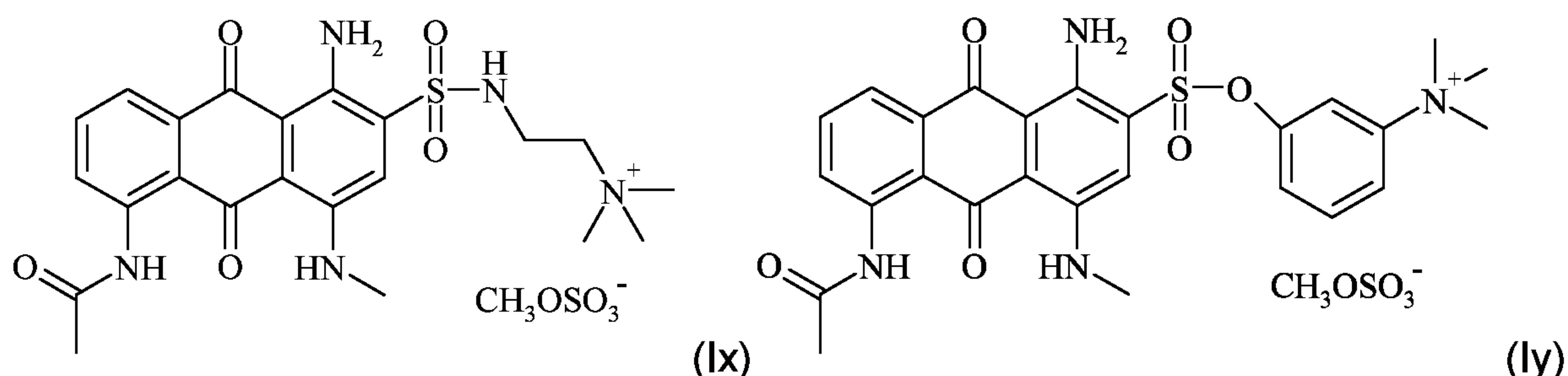


- 10 Still further especially preferred dye compositions of the present invention comprise one or more dyestuffs of the general formula (I) in which
- R is hydrogen or (C_1-C_6) -alkyl;
- T and R^1 are hydrogen;
- Z is $-NR^{51}R^{52}$ or $-NHC(O)R^{56}$, wherein R^{51} is hydrogen and R^{52} is hydrogen or
- 15 (C_1-C_6) -alkyl and R^{56} is (C_1-C_6) -alkyl or phenyl;
- Y is $-NR^{51}R^{52}$, wherein R^{51} is hydrogen, R^{52} is (C_1-C_6) -alkyl, hydroxy- (C_1-C_6) -alkyl or phenyl;
- X is $-OR^{230}$, $-SO_2NR^{270}R^{280}$ or $-SO_2OR^{310}$, wherein R^{230} and R^{310} are (C_1-C_6) -alkyl substituted by Q, hydroxy (C_1-C_6) -alkyl substituted in the alkyl group by Q, phenyl
- 20 substituted by Q; R^{270} is hydrogen, R^{280} is (C_1-C_6) -alkyl substituted by Q or hydroxy (C_1-C_6) -alkyl substituted in the alkyl group by Q;
- Q is a tris (C_1-C_6) -alkyl-ammonium group, a bis (C_1-C_6) -alkyl-benzyl-ammonium group, a methyl-morpholinium group or a methyl-pyrrolidinium group; and

A^- is chloride, sulfate, hydrogensulfate, methylsulfate, ethylsulfate, phosphate, formate, acetate or lactate.

Examples of dyestuffs of this type are the dyestuffs of the formulae (Ix) and (Iy):

5



Still further especially preferred dye compositions of the present invention comprise

one or more dyestuffs of the general formula (I) in which

Y, T and R^1 are hydrogen;

R is hydrogen or (C_1-C_6) -alkyl;

Z is $-NR^{51}R^{52}$ or $-NHC(O)R^{56}$, wherein R^{51} is hydrogen and R^{52} is hydrogen or (C_1-C_6) -alkyl and R^{56} is (C_1-C_6) -alkyl or phenyl;

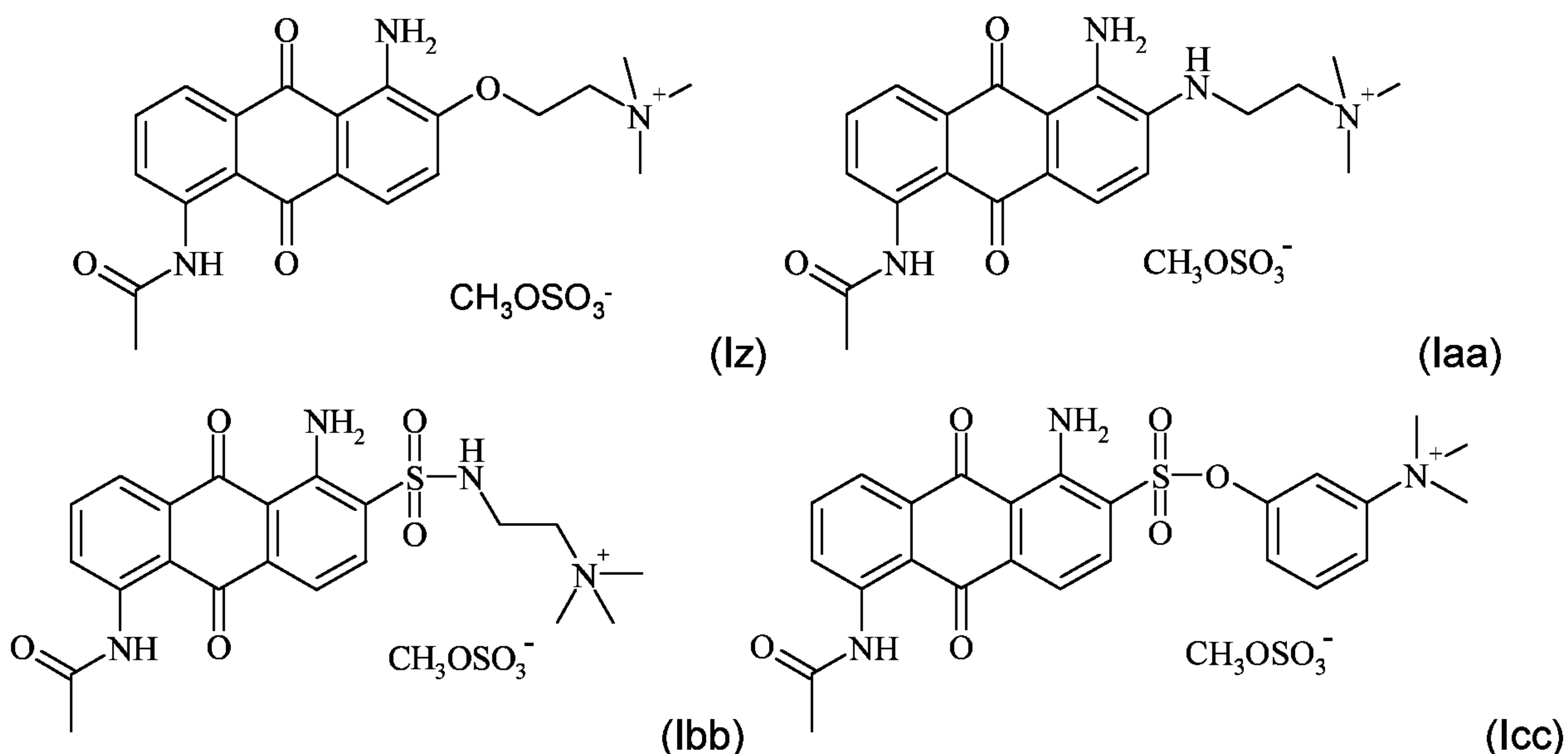
X is $-OR^{230}$, $-SO_2NR^{270}R^{280}$, $-SO_2OR^{310}$ or $-NR^{250}R^{260}$, wherein R^{230} and R^{310} are (C_1-C_6) -alkyl substituted by Q, hydroxy- (C_1-C_6) -alkyl substituted in the alkyl group by Q, or phenyl substituted by Q; R^{27} is hydrogen, R^{28} is (C_1-C_6) -alkyl substituted by Q or hydroxy- (C_1-C_6) -alkyl substituted in the alkyl group by Q; R^{25} is hydrogen and R^{26} is (C_1-C_6) -alkyl substituted by Q;

Q is a tris(C_1-C_6)-alkyl-ammonium group, a bis(C_1-C_6)-alkyl-benzyl-ammonium group, a methyl-morpholinium group or a methyl-pyrrolidinium group which is bonded to X; and

A^- is chloride, sulfate, hydrogensulfate, methylsulfate, ethylsulfate, phosphate, formate, acetate or lactate.

25

Examples of dyestuffs of this type are the dyestuffs of the formulae (Iz), (Iaa), (Ibb) and (Icc):



Still further especially preferred dye compositions of the present invention comprise

one or more dyestuffs of the general formula (I) in which

R is hydrogen or $(\text{C}_1\text{-C}_6)\text{-alkyl}$;

Z is $-\text{NR}^{51}\text{R}^{52}$ wherein R^{51} is hydrogen and R^{52} is hydrogen or $(\text{C}_1\text{-C}_6)\text{-alkyl}$;

Y is OR^{53} , wherein R^{53} is hydrogen;

X is hydrogen,

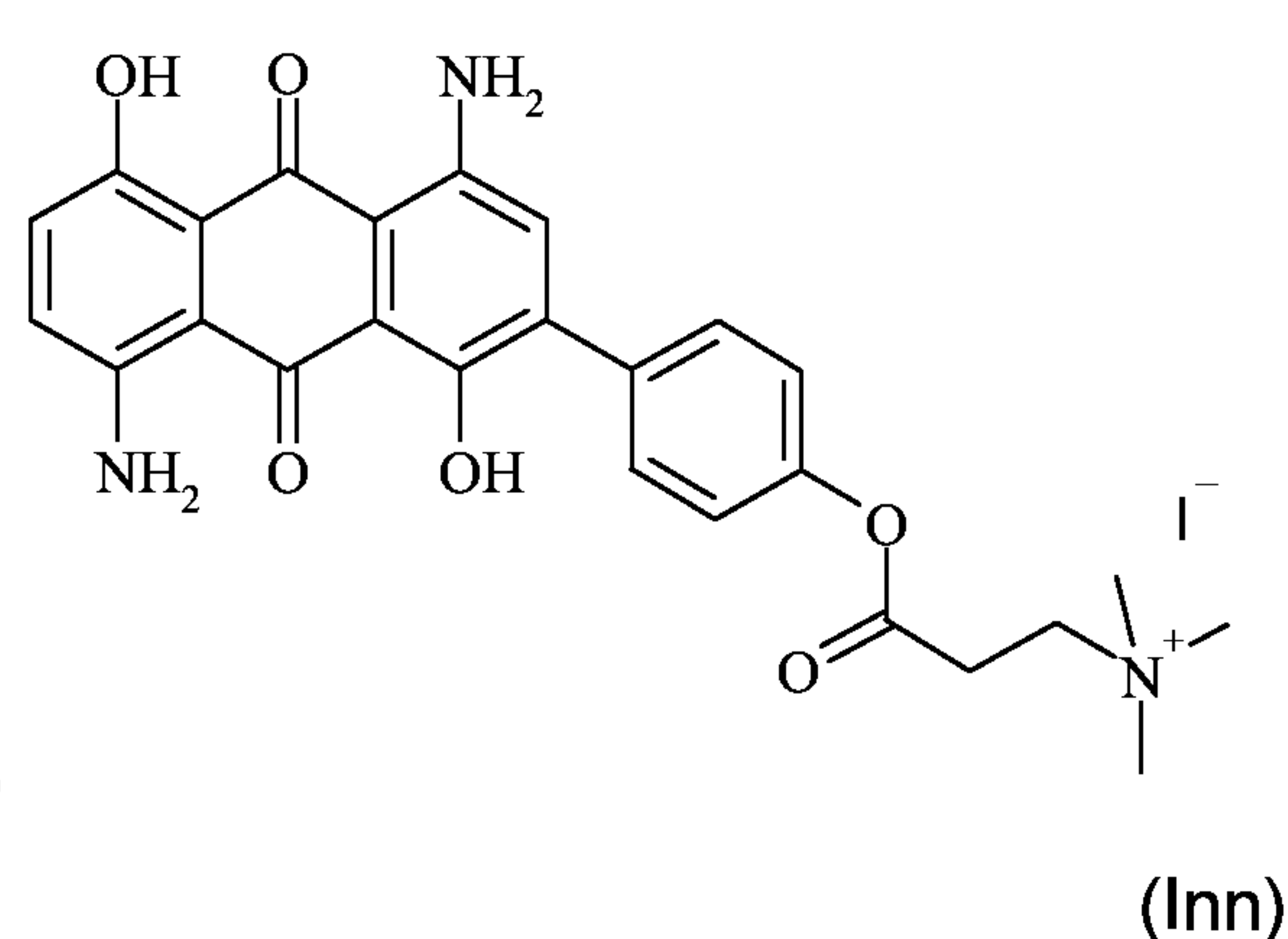
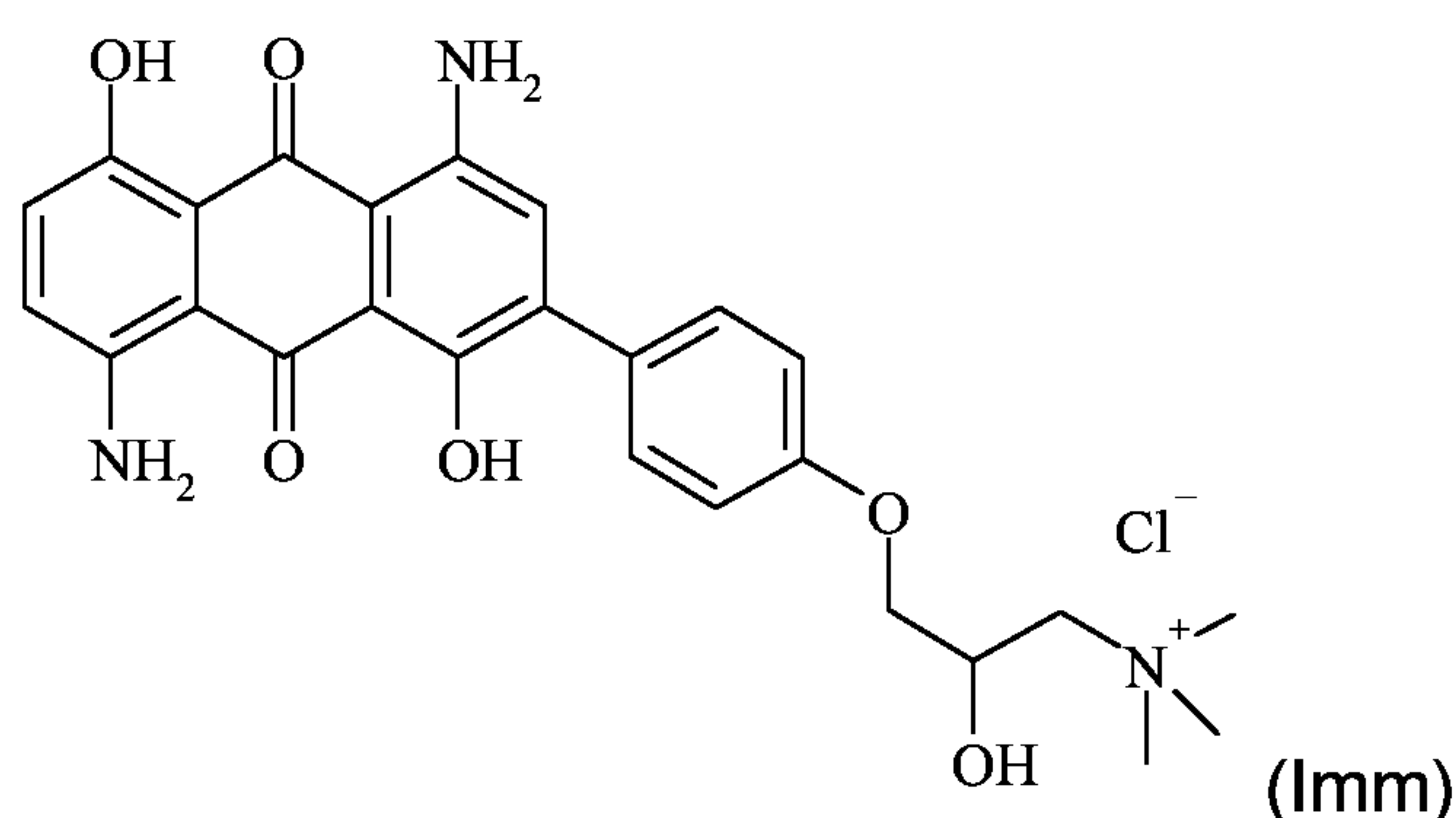
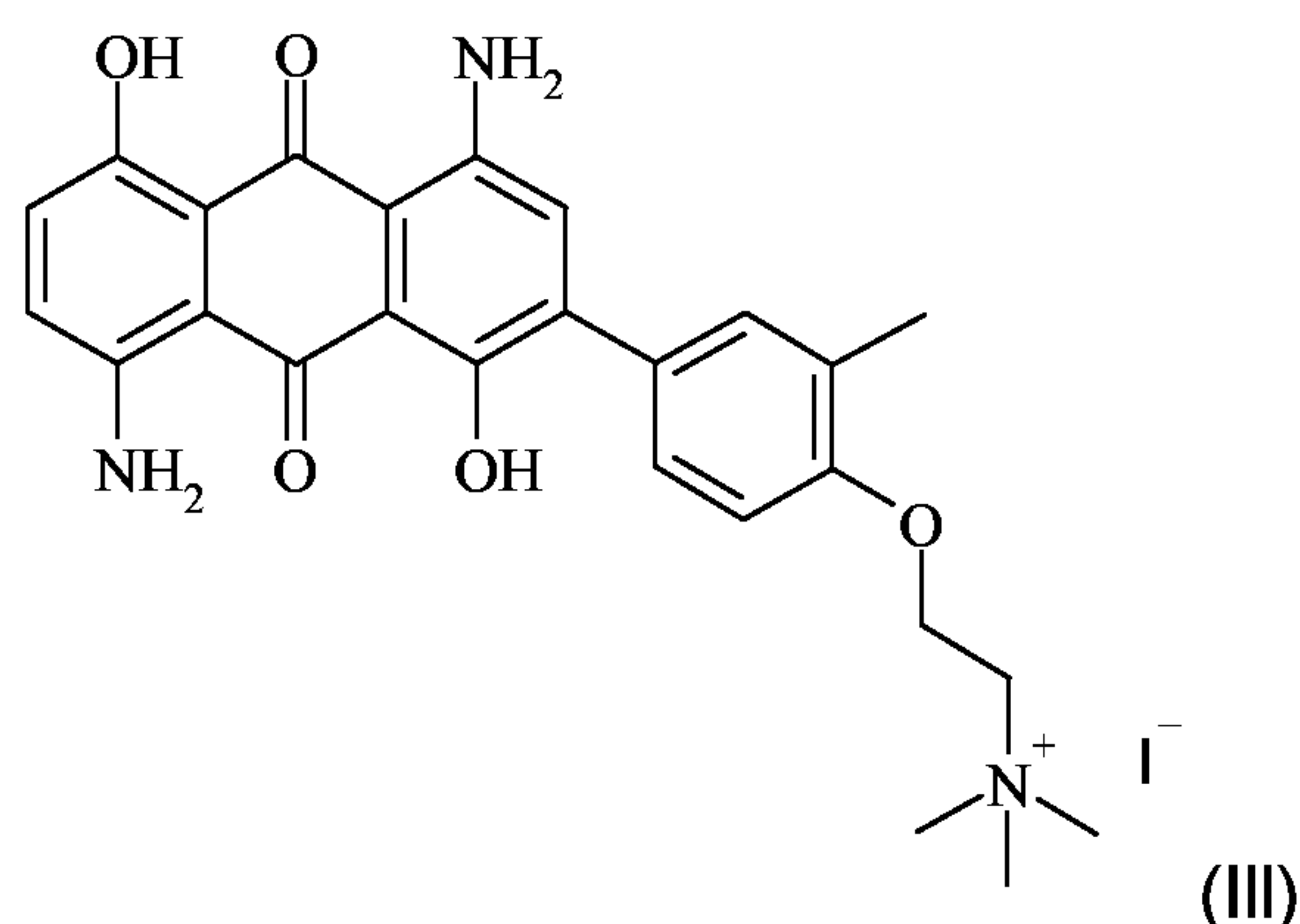
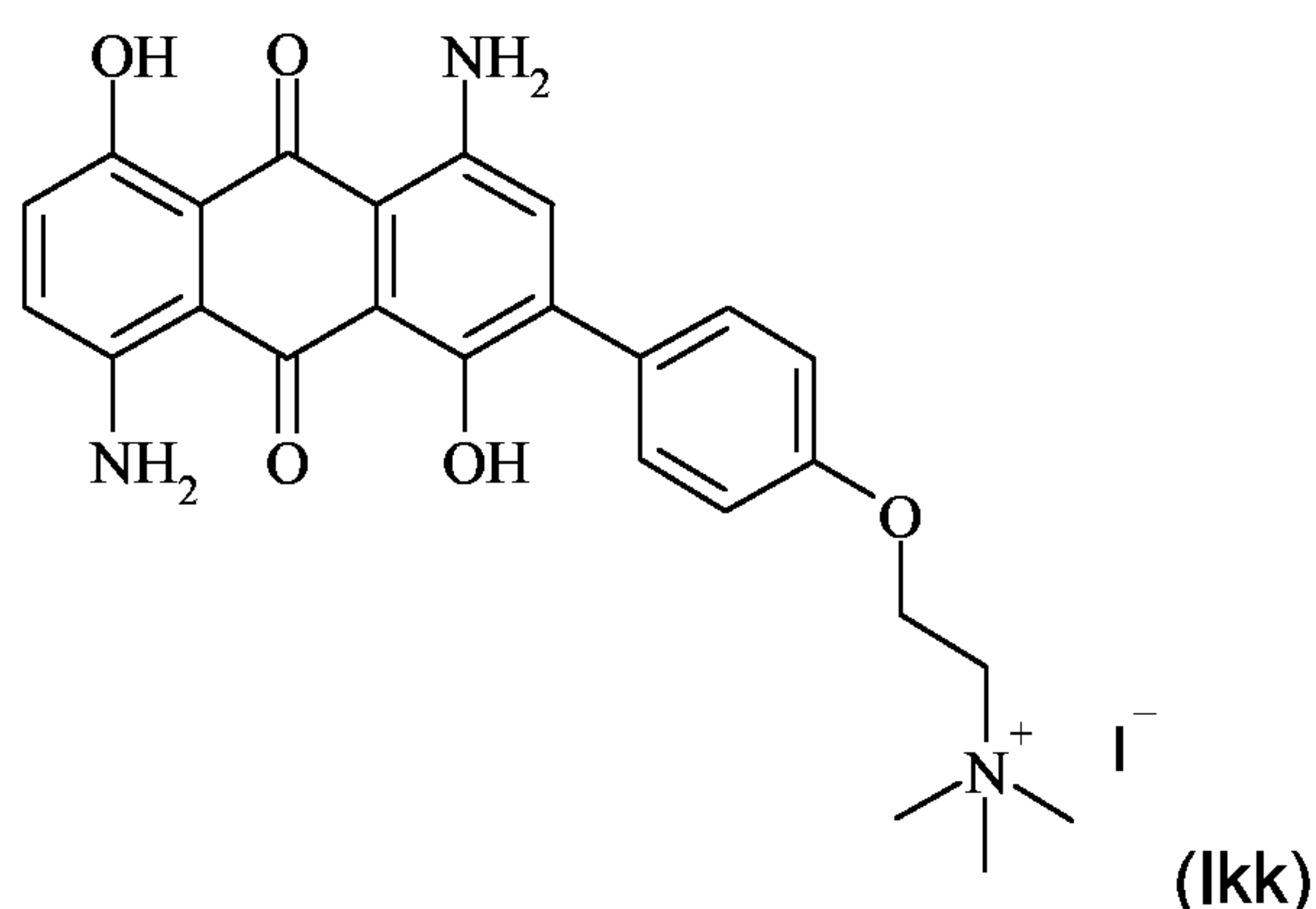
R^1 is $-\text{NH}_2$ or $-\text{NH-alkyl}$;

T is alkyl substituted by Q or aryl substituted by $-\text{OR}^{230}$; wherein R^{230} is $(\text{C}_1\text{-C}_6)\text{-alkyl}$ substituted by Q, hydroxy $(\text{C}_1\text{-C}_6)\text{-alkyl}$ substituted in the alkyl group by Q, $-\text{C}(\text{O})\text{R}^{600}$ or $-\text{SO}_2\text{R}^{900}$ wherein R^{600} and R^{900} are $(\text{C}_1\text{-C}_6)\text{-alkyl}$ substituted by Q or hydroxy $(\text{C}_1\text{-C}_6)\text{-alkyl}$ substituted in the alkyl group by Q;

Q is a tris $(\text{C}_1\text{-C}_6)\text{-alkyl-ammonium}$ group, a bis $(\text{C}_1\text{-C}_6)\text{-alkyl-benzyl-ammonium}$ group, a methyl-morpholinium group or a methyl-pyrrolidinium group; and

A^- is chloride, sulfate, hydrogensulfate, methylsulfate, ethylsulfate, phosphate, formate, acetate or lactate.

Examples of dyestuffs of this type are the dyestuffs of the formulae (Ikk) to (Inn):

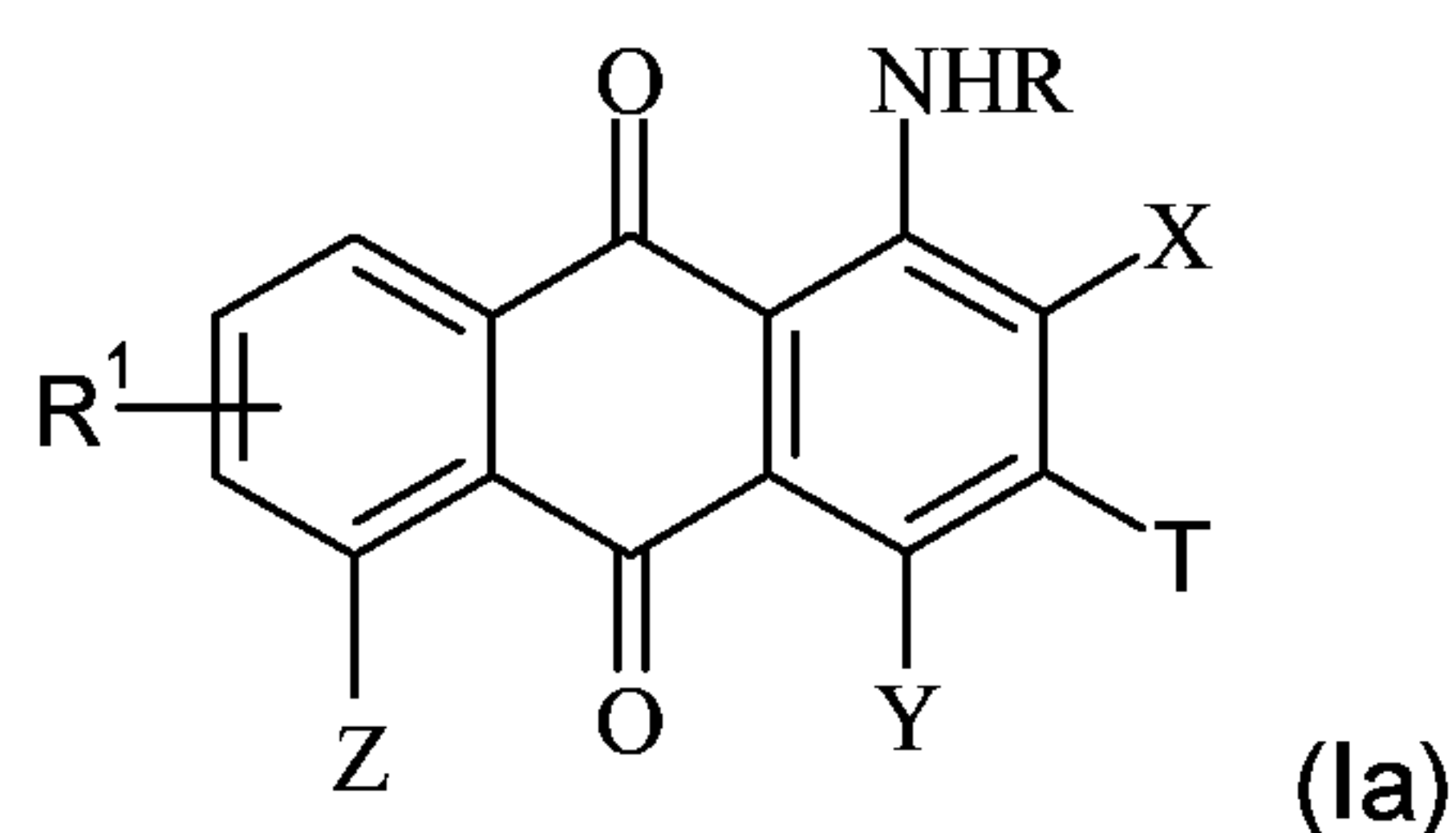


5

The dyestuffs of the formula (I) are partly known from for example US 2,737,517, US 2,888,467, CH 463666, FR 1,363,216 or DE 16 19 365.

Dyestuffs of the below defined formula (Ia), however, are still novel.

10 Accordingly, the present invention provides dyestuffs of the general formula (Ia)



wherein

R is hydrogen, alkyl, alkyl substituted by $-OR^2$, $-SR^3$ or $-NR^5R^4$, hydroxyalkyl, polyhydroxyalkyl, cycloalkyl, aryl substituted by R^{10} , $R^{11}O$ -alkyl, $-OR^{12}$, $-SR^{13}$, $-NR^{14}R^{15}$, $-CONR^{15}R^{16}$, $-C(O)OR^{17}$, $-SO_2-NR^{18}R^{19}$, $-SO_2OR^{20}$, $-C(O)R^{21}$ or $-SO_2R^{22}$, $-C(O)R^6$, $-SO_2NR^7R^8$ or $-SO_2R^9$;

X is hydrogen, $-OR^{235}$, $-SO_2NR^{270}R^{280}$ or $-SO_2OR^{310}$;

Y is hydrogen, $-NR^{51}R^{52}$, $-OR^{53}$, $-SR^{54}$, $-SO_2NHR^{55}$, $-NHC(O)R^{56}$, $-SO_2OR^{57}$,

$-\text{NHSO}_2\text{R}^{58}$, $-\text{SO}_2\text{R}^{59}$, $-\text{NHSO}_2\text{NR}^{60}\text{R}^{61}$, halogen or NO_2 ;

Z is hydrogen, $-\text{NR}^{51}\text{R}^{52}$, $-\text{OR}^{53}$, $-\text{SR}^{54}$, $-\text{SO}_2\text{NHR}^{55}$, $-\text{NHC}(\text{O})\text{R}^{56}$, $-\text{SO}_2\text{OR}^{57}$, $\text{NHSO}_2\text{R}^{58}$, $-\text{SO}_2\text{R}^{59}$, $-\text{NHSO}_2\text{NR}^{60}\text{R}^{61}$, halogen or NO_2 ;

T is hydrogen or aryl substituted by $-\text{OR}^{230}$;

5 R^1 is hydrogen, $-\text{OH}$, $-\text{NH}_2$, $-\text{NHalkyl}$ or NO_2 ;

R^{235} is aryl substituted by $-\text{SO}_2-\text{NR}^{180}\text{R}^{190}$ or $-\text{SO}_2\text{R}^{220}$;

and Q, R^2 to R^{22} , R^{51} to R^{61} , R^{100} , R^{110} , R^{120} , R^{130} , R^{140} , R^{150} , R^{160} , R^{170} , R^{180} , R^{190} , R^{200} , R^{210} , R^{220} , R^{230} , R^{270} , R^{280} and R^{310} are defined as given above.

10 In preferred dyestuffs of the formula (Ia)

Z is hydrogen or amino;

R^1 is hydrogen or hydroxy;

R is hydrogen;

Y is hydroxy or amino; and

15 X is $-\text{OR}^{235}$, wherein R^{235} is $(\text{C}_1\text{-C}_6)\text{-alkyl-NH-SO}_2\text{-phenyl}$, wherein the alkyl group is substituted by Q; and

T is hydrogen or aryl substituted by $-\text{OR}^{230}$, wherein R^{230} is $(\text{C}_1\text{-C}_6)\text{-alkyl}$ substituted by Q, hydroxy $(\text{C}_1\text{-C}_6)\text{-alkyl}$ substituted in the alkyl group by Q, $-\text{C}(\text{O})\text{R}^{600}$ or $-\text{SO}_2\text{R}^{900}$, wherein R^{600} and R^{900} are $(\text{C}_1\text{-C}_6)\text{-alkyl}$ substituted by Q or hydroxy-

20 $(\text{C}_1\text{-C}_6)\text{-alkyl}$ substituted in the alkyl group by Q.

Especially preferred dyestuffs of the formula (Ia) are the dyestuffs (Ii), (Is) and (Ikk) to (Inn).

The dyestuffs of the general formula (I) can be obtained by generally known

25 methods, for instance via Ullmann type substitutions of anthraquinone derivatives which contain exchangeable atoms or groups such as halogen, sulfonic acid group or nitro group by aliphatic amines, aromatic amines, alcohols, phenols, thiols, thiophenols and sulfur containing reagents. General procedures are described, for example, in "Ullmann's Encyclopedia of Industrial Chemistry", VCH

30 Verlagsgesellschaft, Weinheim 1985, volume A2, Anthraquinone Dyes and Intermediates, pages 357–412. The preparing reactions of the dyestuffs can be carried out in an organic solvent such as dimethylformamide, dimethylacetamide, halogenobenzenes etc., in water or preferably in surplus reagent. It is of advantage to carry out the reactions at elevated temperatures, preferably between 60 °C and

150 °C. Acid-binding agents must be added or an excess of amine is used. Adding usual catalysts such as copper or copper salts or mixtures thereof can be advantageously.

The alkoxyanthraquinones of the general formula (I) can be obtained via the conversion of anthraquinonesulfonic acids by alcoholic alkali at 50-130 °C. The direct replacement of halogen to alkoxy- or aryloxyanthraquinones can be advantageously carried out with e.g. alcoholate or phenolate generated in situ with alkali or advantageously with metallic sodium. It is advantageously to carry out these reactions under water free conditions with dried reagents.

Preferred hair dye compositions according to the present invention comprise dyestuff mixtures comprising one or more dyestuffs of the general formula (I) and one or more direct or oxidation dyestuff.

Examples of such direct dyes include dyes from the publicly available dyestuff list

issued by The European Cosmetic, Toiletry and Perfumery Association (COLIPA)

and especially Acid Yellow 1, Disperse Red 17, Basic Brown 17, Acid Black I, 4-Nitro-o-phenylenediamine, Picramic acid, HC Red 13, N,N-bis(2-hydroxyethyl)-2-nitro-p-phenylenediamine, HC Red 7, HC Blue 2, HC Yellow 4, HC Yellow 2, HC Orange 1, HC Red 1, HC Red 3, 4-Amino-3-nitrophenol, 2-Hydroxyethylamino-5-

nitroanisole, 3-Nitro-p-hydroxyethylaminophenol, 3-Methylamino-4-nitrophenoxymethanol, 2-nitro-5-glyceryl methylaniline, HC Violet 1, HC Orange 2, HC Yellow 9, 4-Nitrophenylaminoethylurea, HC Red 10, HC Red 11, 2-Hydroxy-ethyl picramic acid, HC Blue 12, Hydroxyethyl-2-nitro-p-toluidine, HC Blue 11, HC Yellow 7, HC Yellow 10, 4-Amino-2-nitrophenylamine-2-carboxylic acid, 2-Chloro-6-

ethylamino-4-nitrophenol, HC Violet 2, 2-Amino-6-chloro-4-nitrophenol, 4-Hydroxypropylamino-3-nitrophenol, HC Yellow 13, 2,6-Diamino-3-((pyridin-3-yl)azo)pyridine, N-(2-nitro-4-aminophenyl)-allylamine, Basic Violet 2, Basic Red 51, Basic Yellow 87, Basic Orange 31, Basic Red 76, Basic Brown 16, Basic Yellow 57, Acid Orange 7, Acid Red 33, Acid Yellow 23, Acid Blue 9, Acid Red 92, Acid Yellow 3, Acid Violet 43, Disperse Violet 1, Acid Blue 62, Disperse Black 9,

Hydroxyanthraquinoneaminopropylmethyl morpholinium methosulfate, Lawsone, HC Blue 14, Curry Red, Acid Red 18, Acid Red 52, Acid Green 25, Disperse Blue 377, Pigment Red 57, HC Blue 15, Tetrabromophenol Blue, Basic Blue 7, Basic Blue 26, Basic Blue 99, Basic Violet 10, Basic Violet 14; cationic dyes as described in

Japanese Patent Laid-Open Nos. 2204/1983, 118832/1997 and Japanese Laid-Open Publications (PCT) Nos. 501322/1996 and 507545/1996 (please check numbers); and methine type cationic dyes having a cyanine structure.

- 5 Preferred inventive hair dye compositions containing mixtures usually contain one ore more dyestuffs of the general formula (I) in an amount 90 to 10 wt.% and one or more direct or oxidation dyestuff in an amount of 10 to 90 wt.% based on the total weight of the dyestuff mixture.

Preferably, they contain one ore more dyestuffs of the general formula (I) in an
10 amount 80 to 20 wt.% and one or more direct or oxidation dyestuff in an amount of 20 to 80 wt.% based on the total weight of the dyestuff mixture.

Especially preferably, the they contain one ore more dyestuffs of the general formula (I) in an amount 65 to 35 wt.% and one or more direct or oxidation dyestuff in an amount of 35 to 65 wt.% based on the total weight of the dyestuff mixture.

- 15 Further preferred hair dye compositions according to the present invention contain the dyestuff of the general formulae (I) in amounts of 0.0001 to 20 wt.%, preferably 0.001 to 20 wt.%, more preferably from 0.01 to 10 wt.% and especially preferably from 0.05 to 5 wt.%, based on the weight of the hair dye composition.

- 20 Hair dye compositions according to the present invention comprising a dyestuff mixture as described above usually have a dyestuff content between 0.001 to 20 wt.%, preferably from 0.01 to 20 wt.%, more preferably from 0.05 to 10 wt.% and especially preferably from 0.1 to 5 wt.%, based on the weight of the hair dye composition.

25

- In the hair dye compositions according to the present invention, the inventive dyestuffs of the general formula (I) exhibit a high storage stability within a wide pH range from 2 to 11, which is a pH range ordinarily employed for hair dyes, so that the hair dye composition of the present invention can be used at any pH in the above-
30 described pH range. Use in a pH range of from 2 or greater is however preferred from the viewpoint of dyeing property. Hair dye compositions of a pH range of 2 to 8 and hair dye compositions of a pH range of 8 to 12 are preferred.

The desired pH value is usually adjusted using an alkali agent. Examples of alkali agents include ammonia, alkanolamines such as monoethanolamine and isopropanolamine or salts thereof, guanidium salts such as guanidine carbonate and hydroxides such as sodium hydroxide. The inventive hair dye compositions contain
5 an alkali agent preferably in an amount of from 0.01 to 20 wt.%, more preferably from 0.1 to 10 wt.%, especially preferably from 0.5 to 5 wt.% based on the total weight of the composition.

Since the dyestuffs of the formula (I) have high stability against oxidizing agents, the inventive hair dye composition may also be applied to hair together with an oxidizing
10 agent. In other words, it can be provided as a two-part composition composed of a first part containing the dyestuff of the general formula (I) and a second part containing an oxidizing agent. In this case, hair dyeing and bleaching can be carried out simultaneously, which facilitates more vivid hair dyeing.

Examples of oxidizing agent include hydrogen peroxide, persulfates such as
15 ammonium persulfate, potassium persulfate and sodium persulfate, perborates such as sodium perborate, percarbonates such as sodium percarbonate and bromates such as sodium bromate and potassium bromate. Hydrogen peroxide is especially preferred from the viewpoints of hair bleaching property, stability and effectiveness of the inventive dyestuffs of the general formula (I). Hydrogen peroxide may be used in
20 combination with another oxidizing agent. The oxidizing agent is preferably used in an amount of from 0.5 to 10 wt.%, especially preferably from 1 to 8 wt.%, based on the hair dye composition.

The first part containing the inventive dyestuff of the general formula (I) and the
25 second part containing the oxidizing agent are mixed at a volume ratio preferably ranging from 2:1 to 1:3.

In the hair dye composition of the present invention, an oxidation dye can be used in combination with the inventive dyestuff of the general formula (I). Such combined use enables considerably vivid and intense dyeing which cannot be accomplished by
30 the single use of the oxidation dye. For the oxidation dye, known developers and couplers ordinarily employed for an oxidation type hair dye can be used.

Examples of the developer include paraphenylenediamine, toluene-2,5-diamine, 2-chloro-paraphenylenediamine, N-methoxyethyl-paraphenylenediamine, N,N-bis(2-hydroxyethyl)-paraphenylenediamine, 2-(2-hydroxyethyl)-paraphenylenediamine, 2,6-

dimethyl-para-phenylenediamine, 4,4'-diaminodiphenylamine, 1,3-bis(N-(2-hydroxyethyl)-N-(4-aminophenyl)amino)-2-propanol, PEG-3,2,2'-paraphenylenediamine, paraaminophenol, paramethylaminophenol, 3-methyl-4-aminophenol, 2-aminomethyl-4-aminophenol, 2-(2-hydroxyethylaminomethyl)-4-aminophenol, orthoaminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 2-amino-5-acetamidophenol, 3,4-diaminobenzoic acid, 5-aminosalicylic acid, 2,4,5,6-tetraaminopyrimidine, 2,5,6-triamino-4-hydroxypyrimidine and 4,5-diamino-1-(4'-chlorobenzyl)pyrazole and salts thereof.

Examples of the coupler include metaphenylenediamine, 2,4-

diaminophenoxyethanol, 2-amino-4-(2-hydroxyethylamino)anisole, 2,4-diamino-5-methylphenetole, 2,4-diamino-5-(2-hydroxyethoxy)toluene, 2,4-dimethoxy-1,3-diaminobenzene, 2,6-bis(2-hydroxyethylamino)toluene, 2,4-diamino-5-fluorotoluene, 1,3-bis(2,4-diaminophenoxy)propane, metaaminophenol, 2-methyl-5-aminophenol, 2-methyl-5-(2-hydroxyethylamino)phenol, 2,4-dichloro-3-aminophenol, 2-chloro-3-amino-6-methylphenol, 2-methyl-4-chloro-5-aminophenol, N-cyclopentyl-metaaminophenol, 2-methyl-4-methoxy-5-(2-hydroxyethylamino)phenol, 2-methyl-4-fluoro-5-aminophenol, resorcin, 2-methylresorcin, 4-chlororesorcin, 1-naphthol, 1,5-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 2-isopropyl-5-methylphenol, 4-hydroxyindole, 5-hydroxyindole, 6-hydroxyindole, 7-hydroxyindole, 6-hydroxybenzomorpholine, 3,4-methylenedioxyphenol, 2-bromo-4,5-methylenedioxyphenol, 3,4-methylenedioxyaniline, 1-(2-hydroxyethyl)amino-3,4-methylenedioxybenzene, 2,6-dihydroxy-3,4-dimethylpyridine, 2,6-dimethoxy-3,5-diaminopyridine, 2,3-diamino-6-methoxypyridine, 2-methylamino-3-amino-6-methoxypyridine, 2-amino-3-hydroxypyridine, and 2,6-diaminopyridine and salts thereof.

As each of the developer and coupler, at least two of the above-described developers or couplers are usable. The content of each of them is preferably from 0.01 to 20 wt.%, especially preferably from 0.05 to 10 wt.% based on the hair dye composition.

To the hair dye composition of the present invention, an autoxidation dye typified by an indole or an indoline, or a known direct dye such as a nitro dye or a disperse dye can also be added.

Addition of a polyol, polyol alkyl ether, cationic or amphoteric polymer and/or silicone to the hair dye composition of the present invention is preferred, because the resulting composition can dye the hair uniformly and provides improved cosmetic effects of the hair.

5

In addition to the above-described components, those ordinarily employed as a raw material for cosmetics can be added to the hair dye composition of the present invention. Examples of such an optional component include hydrocarbons, animal or vegetable fats and oils, higher fatty acids, organic solvents, penetration promoters, cationic surfactants, natural or synthetic polymers, higher alcohols, ethers, amphoteric surfactants, nonionic surfactants, anionic surfactants, protein derivatives, amino acids, antiseptics, chelating agents, stabilizers, antioxidants, plant extracts, crude drug extracts, vitamins, colorants, perfumes and ultraviolet absorbers.

10

15

The hair dye composition of the present invention can be prepared in a conventional manner to form a one-part composition or a two-part composition having a first part containing an alkali agent and a second part containing an oxidizing agent. The inventive dyestuff of the general formula (I) may be incorporated in at least one of these parts of the two-part or three-part composition. When the hair dye composition of the present invention is of the one-part type, it is applied to the hair directly, while when it is of the two- or three-part type, these parts are mixed just before hair dyeing and the mixture is applied to the hair.

20

25

In the case of preparation of a two-part type hair dye composition, the first part is typically prepared by mixing the Inventive dyestuff of the general formula (I) and optionally an oxidation dye and adjusting the pH of the mixture to 8 to 12 with an alkali agent such as ammonia. The second part is prepared by incorporating about 2 to 6 wt.% of hydrogen peroxide, adjusting the mixture to weakly acidic with phosphoric.

30

The hair dye composition of the present invention can be provided in the form of powder, transparent liquid, emulsion, cream, gel, paste, aerosol, aerosol foam or the like. It preferably has a viscosity of 2000 to 100000 mPa·s upon its application to the hair (after mixing of all the parts when the composition is a two-part or three-part type). The above-described viscosity is measured at 20°C by using a Brookfield rotary viscometer (No. 5 spindle, 5 rpm).

The present invention also refers to a process for colouring hair characterized in that a hair dye composition as described above is applied onto hair, left for 1 to 45 minutes and then rinsed off from hair.

- 5 In a preferred inventive process the hair dye composition is mixed with a composition comprising at least one oxidizing agent.

In the following, embodiments of the invention are described in detail for the purpose of illustrating only and not for the purpose of limiting the same.

10

Preparation of dyestuffs

a) Preparation of ([2-(1-amino-4-hydroxy-9,10-dioxo-9,10-dihydro-anthracen-2-ylsulfanyl)-ethyl]-trimethyl-ammonium methylsulfate)

- 15 5.0 parts of sulfur, 14.0 parts of sodium sulfide hydrate are dissolved in 80 parts of ethyl alcohol at 50–60 °C. Thereafter 10 parts of 1-amino-2-bromo-4-hydroxy-anthraquinone were added and the reaction mixture was kept for 5 hours under reflux. After cooling off and acidification with 100 parts of 2N HCl, the precipitate was filtered off and washed with water. Upon drying 14.3 parts of a red powder were
20 obtained. The isolated product was taken in 250 parts of 3 % sodium hydroxide solution, stirred for 20 minutes and filtered off. The sulfur-free filtrate was treated further with 7.7 parts of 2-dimethylaminoethyl chloride hydrochloride and the solution was heated at reflux for 7 hours. After cooling off, the pH was adjusted to ca. 9.0 with conc. HCl and the precipitate was filtered off, washed and dried to give 10.1 parts of
25 product. For the quaternisation the isolated dye was dispersed in 75 parts of chlorobenzene and treated with 3.3 parts of dimethylsulfate. The mixture was stirred at 30 °C for 1 hour and thereafter for another hour at 40 °C. After cooling at room temperature the precipitate was filtered off and washed with acetone. Upon drying 11.7 parts of the dye of formula Ig were obtained. The reddish violet dye Ig is very
30 good water-soluble. The analytic data are consistent with the assigned structure for dye Ig.

Melting point: > 204 °C;

λ_{max} (H₂O) = 535 nm (9100).

b) Preparation of ([2-(1,4-diamino-9,10-dioxo-9,10-dihydro-anthracen-2-yloxy)-ethyl]-trimethyl-ammonium methylsulfate)

5 15 parts of 1,4-diamino-9,10-dioxo-9,10-dihydro-anthracene-2-sulfonic acid, 100 parts of 2-dimethylamino-ethanol and 15 parts of solid KOH were heated together at 80 °C and kept at this temperature for 1 hour. After cooling off, mixture was poured into 500 parts of cold water. The precipitate was filtered off, washed with water and dried to yield a reddish violet powder. 2.5 parts of the dyestuff thus obtained were
10 dispersed in 50 parts of chlorobenzene and treated with 1.0 part of dimethylsulfate. The reaction mixture was stirred at 40 °C for 3½ hours. The precipitate was filtered off at 30 °C and washed with acetone. Upon drying 3.3 parts of the dye of formula Ih were obtained. The reddish violet dye Ih is very good water-soluble. The analytic data are consistent with the assigned structure for dye Ih.

15 Melting point: > 223 °C;

λ_{\max} (H₂O) = 533 nm (9200), 569 nm (9000).

c) Preparation of ({3-[4-(1-amino-4-hydroxy-9,10-dioxo-9,10-dihydro-anthracen-2-yloxy)-benzenesulfonylamino]-propyl}-trimethyl-ammonium methylsulfate)

20

30 parts of 4-(1-amino-4-hydroxy-9,10-dioxo-9,10-dihydro-anthracen-2-yloxy)benzenesulfonyl chloride were dispersed in 160 parts of acetonitrile. 20 parts of 3-dimethylaminopropylamine were added dropwise. After stirring 4 hours at room temperature, the reaction mixture was filtered off, washed with water and dried to
25 yield 35.0 parts of a dark red powder. 10.0 parts of the dye thus obtained were dispersed in 100 parts of chlorobenzene and treated with 2.4 parts of dimethylsulfate. The reaction mixture was stirred at 40 °C for 3 hours. The precipitate was filtered off and washed with acetone. Upon drying 10.6 parts of the dye of the formula li were obtained. The red dye li is very good water-soluble. The analytic data
30 are consistent with the assigned structure for dye li.

Melting point: > 145 °C;

λ_{\max} (H₂O) = 521 nm (12200), 550 nm (shoulder, 9600).

d) Preparation of ([2-(1-amino-4-methanesulfonylamino-9,10-dioxo-9,10-dihydro-anthracen-2-yloxy)-ethyl]-trimethyl-ammonium methylsulfate)

5.7 parts of N-[4-amino-3-(2-dimethylamino-ethoxy)-9,10-dioxo-9,10-dihydro-anthracen-1-yl]-methanesulfonamide, prepared from 1-amino-4-methanesulfonylamino-9,10-dioxo-9,10-dihydro-anthracene-2-sulfonic acid, N,N-dimethylaminoethanolamine and potassium hydroxide at 60 °C, were dispersed in 50 parts of chlorobenzene and treated with 1.7 parts of dimethylsulfate. The reaction mixture was stirred at room temperature for 5 hours. The precipitate was filtered off and washed with acetone. Upon drying 5.8 parts of the dye of the formula Idd were obtained. The red dye Idd is very good water-soluble. The analytic data are consistent with the assigned structure for dye Idd.

Melting point: > 206 °C;

λ_{\max} (H₂O) = 515 nm (9000).

e) Preparation of ([2-(5-acetylamino-1-amino-9,10-dioxo-9,10-dihydro-anthracen-2-yloxy)-ethyl]-trimethyl-ammonium methylsulfate)

5.5 parts of N-[5-amino-6-(2-dimethylamino-ethoxy)-9,10-dioxo-9,10-dihydro-anthracen-1-yl]-acetamide, prepared from 5-acetylamino-1-amino-9,10-dioxo-9,10-dihydro-anthracene-2-sulfonic acid, N,N-dimethylaminoethanolamine and potassium hydroxide at 60 °C, were dispersed in 75 parts of chlorobenzene and treated with 1.7 parts of dimethylsulfate. The reaction mixture was stirred at room temperature for 5 hours. The precipitate was filtered off and washed with acetone. Upon drying 4.8 parts of the dye of the formula Iz were obtained. The red dye Iz is very good water-soluble. The analytic data are consistent with the assigned structure for dye Iz.

Melting point: > 280 °C;

λ_{\max} (MeCN) = 487 nm (18300).

Preparation of hair dye compositions

Example A

The dyes listed in Table 1 below were dissolved into Base Formulation 1 together with the compounds as follows:

5	Dyestuff of general formula (I)	0.5g
	iso-Propanol	5.0g
	Ammonium Hydroxide (25%)	5.0g
	Water	up to 100g
	pH	10.2

10

Example B

The dyes listed in Table 2 below were dissolved into Base Formulation 2 together with the compounds as follows:

	Dyestuff of general formula (I)	0.5g
15	iso-Propanol	5.0g
	Ammonium Hydroxide (25%)	5.0g
	Hydrogen Peroxide (50%)	6.0g
	Water	up to 100g
	pH	10.2

20

Dyeing Performance

a) Approximately 1.5 g of the Base Formulation I was applied to 1g of undamaged white goat hair at 30°C for 30mins. At the end of the processing time the tresses were rinsed with water, shampooed and then dried.

25 The color of the tresses was recorded by measuring L, a and b values of the tresses before and after the colouring using a hand held Datacolor Mercury colour-measuring instrument and the value of delta E, which is a known measure for the chroma, was calculated according to the well-known equation: $\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$ for each example (this will apply equally to every example hereinafter).

30

The results are shown in Table 1

Table 1

Dyestuff	Color of Dyed Hair	L	a	b	Delta E
Formula li	Pure Magenta	53.9	30.3	-5.7	45.0
Formula Ig	Intense Violet	40.3	23.2	-13.9	54.7
Formula Ih	Brilliant Purple	42.5	23.8	-20.8	57.7
Formula Idd	Intense Blue-Red	54	28.9	-0.52	41.8
Formula Ic	Intense Purple	47.3	20.5	-16	50.9

b) Approximately 1.5 g of the Base Formulation 2 was applied to 1g of undamaged white goat hair at 30°C for 30mins. At the end of the processing time the tresses
5 were rinsed with water, shampooed and then dried. The color of the tresses was recorded as given in Example A above.

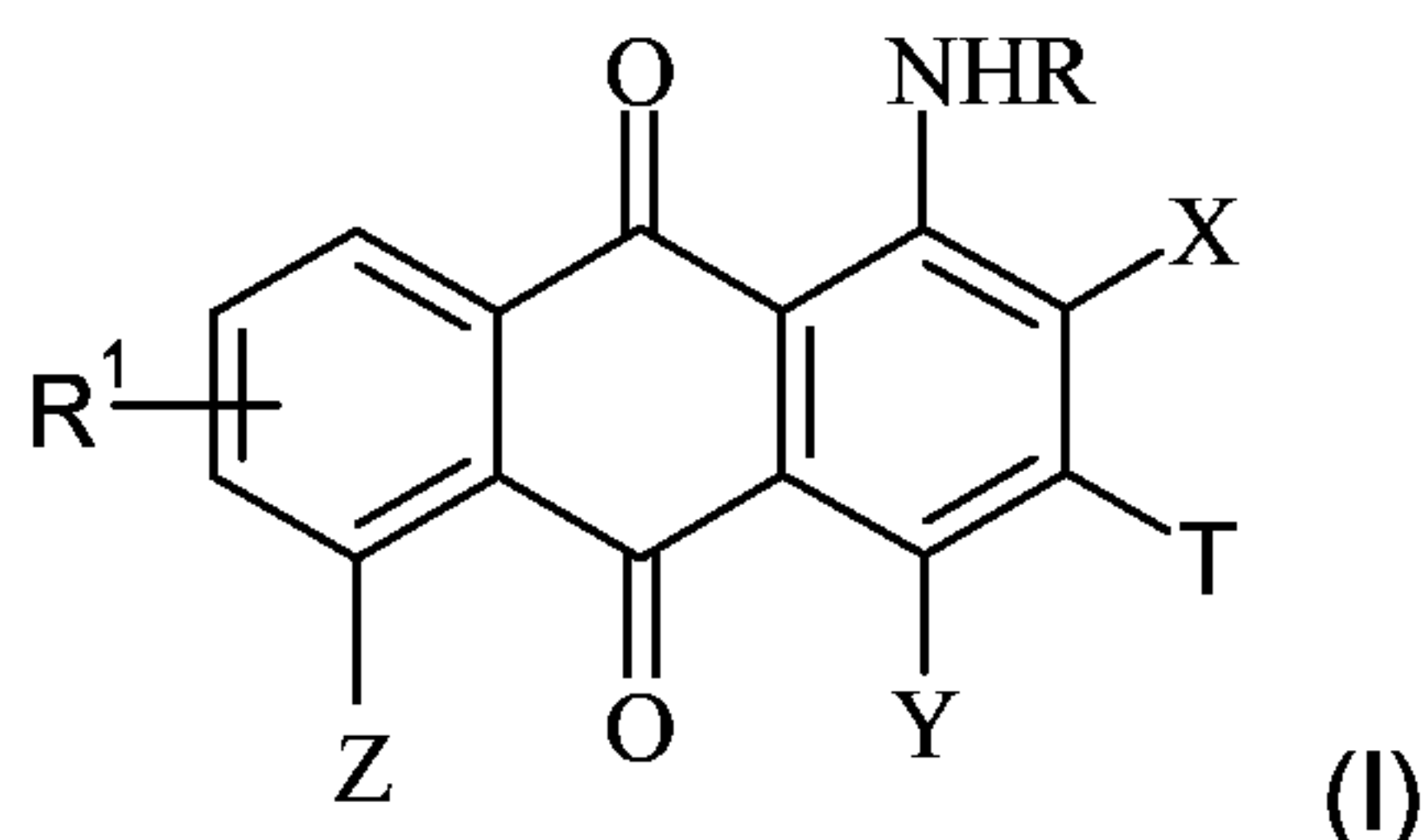
The results are shown in Table 2

10 Table 2

Dyestuff	Color of Dyed Hair	L	a	b	Delta E
Formula li	Pure Magenta	53.9	30.3	-5.7	45.0
Formula Ig	Intense Violet	40.3	23.2	-13.9	54.7
Formula Ih	Brilliant Purple	42.5	23.8	-20.8	57.7
Formula Idd	Intense Blue-Red	51.9	33.8	-0.63	46.6
Formula Ic	Intense Purple	57.9	20.1	-11.6	39.5

Claims

1. Hair dye composition comprising one or more dyestuffs of the general formula (I)



5 wherein

R is hydrogen, alkyl, alkyl substituted by $-OR^2$, $-SR^3$ or $-NR^5R^4$, hydroxyalkyl, polyhydroxyalkyl, cycloalkyl, aryl substituted by R^{10} , $R^{11}O$ -alkyl, $-OR^{12}$, $-SR^{13}$, $-NR^{14}R^{15}$, $-CONR^{15}R^{16}$, $-C(O)OR^{17}$, $-SO_2-NR^{18}R^{19}$, $-SO_2OR^{20}$, $-C(O)R^{21}$ or $-SO_2R^{22}$, $-C(O)R^6$, $-SO_2NR^7R^8$ or $-SO_2R^9$;

10

X is hydrogen, $-OR^{230}$, $-SR^{240}$, $-NR^{250}R^{260}$, $-SO_2NR^{270}R^{280}$, $-CONR^{290}R^{300}$, $-SO_2OR^{310}$, $-C(O)OR^{320}$, $-C(O)R^{330}$, $-SO_2R^{340}$, alkyl substituted by Q, $-OR^{201}$, $-SR^{300}$ or $-NR^{500}R^{400}$, aryl substituted by R^{100} , $R^{110}O$ -alkyl, $-OR^{120}$, $-SR^{130}$, $-NR^{140}R^{150}$, $-CONR^{150}R^{160}$, $-C(O)OR^{170}$, $-SO_2-NR^{180}R^{190}$, $-SO_2OR^{200}$, $-C(O)R^{210}$ or $-SO_2R^{220}$, $-NHSO_2R^{360}R^{370}$ or $-CH=NR^{350}$;

15

T is hydrogen, alkyl substituted by Q or aryl substituted by $-OR^{230}$;

Y is hydrogen, $-NR^{51}R^{52}$, $-OR^{53}$, $-SR^{54}$, $-SO_2NHR^{55}$, $-NHC(O)R^{56}$, $-SO_2OR^{57}$, $-NHSO_2R^{58}$, $-SO_2R^{59}$, $-NHSO_2NR^{60}R^{61}$, halogen or NO_2 ;

20

Z is hydrogen, $-NR^{51}R^{52}$, $-OR^{53}$, $-SR^{54}$, $-SO_2NHR^{55}$, $-NHC(O)R^{56}$, $-SO_2OR^{57}$, $-NHSO_2R^{58}$, $-SO_2R^{59}$, $-NHSO_2NR^{60}R^{61}$, halogen or NO_2 ;

25 R^1 is hydrogen, $-OH$, $-NH_2$, $-NH$ alkyl or NO_2 ;

each of R^2 to R^8 , R^{60} and R^{61} , independently, is hydrogen, alkyl, aryl, hydroxyalkyl, polyhydroxyalkyl or cycloalkyl;

R^9 is alkyl, aryl, hydroxyalkyl, polyhydroxyalkyl or cycloalkyl;

30

each of R^{10} to R^{21} , independently, is hydrogen, alkyl, hydroxyalkyl, polyhydroxyalkyl or cycloalkyl;

R^{22} is alkyl, hydroxyalkyl, polyhydroxyalkyl or cycloalkyl;

5

each of R^{51} to R^{54} , independently, is hydrogen, alkyl, hydroxyalkyl, polyhydroxyalkyl, cycloalkyl, cycloalkyl substituted by $-C(O)R^6$, $-SO_2R^9$, or aryl substituted by R^{10} , $R^{11}O$ -alkyl, $-OR^{12}$, $-SR^{13}$, $-NR^{14}R^{15}$, $-CONR^{15}R^{16}$, $-C(O)OR^{17}$, $-SO_2-NR^{18}R^{19}$, $-SO_2OR^{20}$, $-C(O)R^{21}$ or $-SO_2R^{22}$;

10

each of R^{55} to R^{57} , independently, is hydrogen, alkyl, hydroxyalkyl, polyhydroxyalkyl, cycloalkyl or aryl substituted by R^{10} , $R^{11}O$ -alkyl, $-OR^{12}$, $-SR^{13}$, $-NR^{14}R^{15}$, $-CONR^{15}R^{16}$, $-C(O)OR^{17}$, $-SO_2-NR^{18}R^{19}$, $-SO_2OR^{20}$, $-C(O)R^{21}$ or $-SO_2R^{22}$;

15

each R^{58} and R^{59} , independently, is alkyl, hydroxyalkyl, polyhydroxyalkyl, cycloalkyl or aryl substituted by R^{10} , $R^{11}O$ -alkyl, $-OR^{12}$, $-SR^{13}$, $-NR^{14}R^{15}$, $-CONR^{15}R^{16}$, $-C(O)OR^{17}$, $-SO_2-NR^{18}R^{19}$, $-SO_2OR^{20}$, $-C(O)R^{21}$ or $-SO_2R^{22}$;

20

each of R^{230} , R^{240} and R^{350} , independently, is alkyl substituted by Q, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl substituted by Q, $-C(O)R^{600}$ or $-SO_2R^{900}$, or aryl substituted by R^{100} , $R^{110}O$ -alkyl, $-OR^{120}$, $-SR^{130}$, $-NR^{140}R^{150}$, $-CONR^{150}R^{160}$, $-C(O)OR^{170}$, $-SO_2-NR^{180}R^{190}$, $-SO_2OR^{200}$, $-C(O)R^{210}$ or $-SO_2R^{220}$;

25

each of R^{201} , R^{200} , R^{600} , R^{900} , independently, is alkyl substituted by Q, aryl substituted by Q, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl substituted by Q,

30

each of R^{100} , R^{110} , R^{120} , R^{130} , R^{170} , R^{200} , R^{210} , R^{220} , independently, is alkyl substituted by Q, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl substituted by Q,

each of R^{140} , R^{150} , R^{160} , R^{180} and R^{190} is hydrogen, alkyl, alkyl substituted by Q, hydroxyalkyl, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl,

polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl or cycloalkyl substituted by Q, with the proviso that each the groups $-NR^{140}R^{150}$, $-CONR^{150}R^{160}$ and $-SO_2-NR^{180}R^{190}$ must contain one group Q;

- 5 each of R^{310} , R^{320} , R^{330} and R^{340} , independently, is alkyl substituted by Q, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl substituted by Q or aryl substituted by R^{100} , $R^{110}O$ -alkyl, $-OR^{120}$, $-SR^{130}$, $-NR^{140}R^{150}$, $-CONR^{150}R^{160}$, $-C(O)OR^{170}$, $-SO_2-NR^{180}R^{190}$, $-SO_2OR^{200}$, $-C(O)R^{210}$ or $-SO_2R^{220}$;

10

each of R^{360} and R^{370} is hydrogen, alkyl, alkyl substituted by Q, aryl, aryl substituted by Q, hydroxyalkyl, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl or cycloalkyl substituted by Q, with the proviso that the group $-NHSO_2R^{360}R^{370}$ must contain one

15 group Q;

- each of R^{250} , R^{260} , R^{270} , R^{280} , R^{290} and R^{300} , independently, is hydrogen, alkyl, alkyl substituted by Q, hydroxyalkyl, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl or cycloalkyl substituted by Q, $-C(O)R^{601}$, $-SO_2R^{901}$, or aryl substituted by R^{101} , $R^{111}O$ -alkyl, $-OR^{121}$, $-SR^{131}$, $-NR^{141}R^{151}$, $-CONR^{151}R^{161}$, $-C(O)OR^{171}$, $-SO_2-NR^{181}R^{191}$, $-SO_2OR^{202}$, $-C(O)R^{211}$ or $-SO_2R^{221}$, with the proviso that each of the groups $-NR^{250}R^{260}$, $-SO_2NR^{270}R^{280}$ and $-CONR^{290}R^{300}$ must contain one group Q;

20

- 25 each of R^{111} , R^{121} , R^{131} , R^{141} , R^{151} , R^{161} , R^{171} , R^{181} , R^{191} , R^{202} and R^{211} , independently, is hydrogen, alkyl, alkyl substituted by Q, hydroxyalkyl, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl or cycloalkyl substituted by Q;

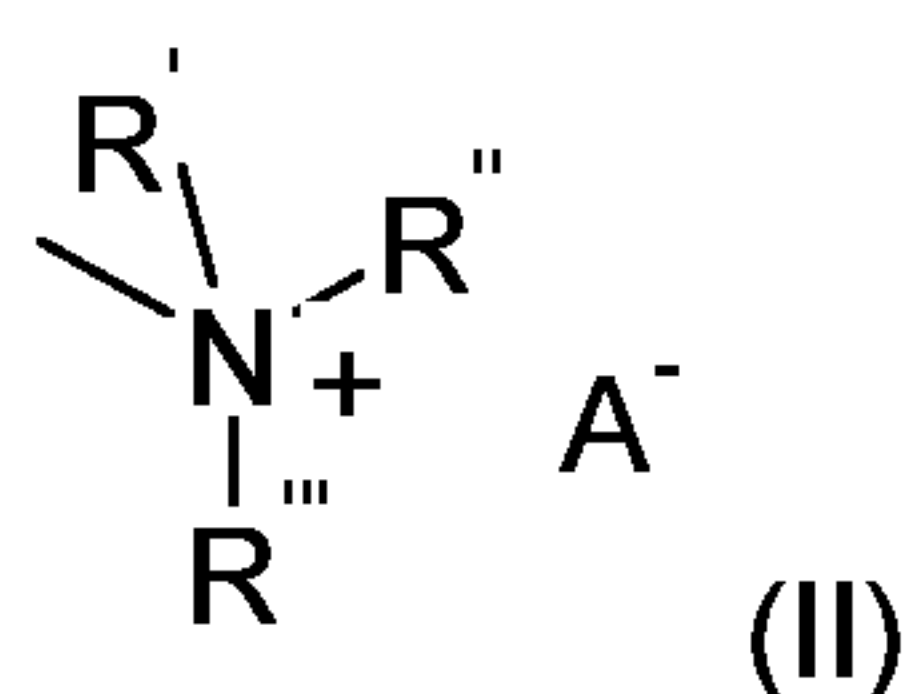
- 30 R^{221} is alkyl, alkyl substituted by Q, hydroxyalkyl, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl or cycloalkyl substituted by Q;

R^{601} is hydrogen, alkyl, alkyl substituted by Q, aryl, aryl substituted by Q, hydroxyalkyl, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl or cycloalkyl substituted by Q; and

5

R^{901} is alkyl, alkyl substituted by Q, aryl, aryl substituted by Q, hydroxyalkyl, hydroxyalkyl substituted in the alkyl group by Q, polyhydroxyalkyl, polyhydroxyalkyl substituted in the alkyl group by Q, cycloalkyl or cycloalkyl substituted by Q; and

10 Q is a group of the general formula (II)



wherein

each of R' , R'' and R''' , independently, is alkyl, aryl, arylalkyl, cycloalkyl, cycloalkylalkyl, heteroaryl, heteroarylalkyl, heterocycloalkyl, heterocycloalkyl-alkyl, either of which can be substituted by heteroatom containing groups or R' and R'' form together with the nitrogen to which they are bonded a 5- or 6- membered heterocyclic ring; and

15

A^- is a cosmetically acceptable anion;

20

whereby the dyestuff of the formula (I) contains exactly one group Q; whereby at least one of the groups Y and Z are groups other than hydrogen; and whereby T and R^1 are hydrogen if X is different from hydrogen.

2. Hair dye composition according to claim 1, wherein in the group of the formula (II)

25

R' , R'' and R''' are (C_1-C_6) -alkyl or benzyl and A^- is chloride, bromide, iodide, hydroxide, hydrogenphosphate, phosphate, carbonate, hydrogencarbonate, hydrogensulfate, perchlorate, fluoroborate, chlorozincate, methylsulfate, ethylsulfate, acetate, propionate, lactate or citrate or a mixture thereof.

30

3. Hair dye composition according to claims 1 and/or 2, wherein in the general formula (I)

Z, T and R¹ are hydrogen;

R is hydrogen or (C₁-C₆)-alkyl;

Y is -NR⁵¹R⁵², -NHSO₂R⁵⁸ or -OR⁵³, wherein R⁵¹ is hydrogen and R⁵² is hydrogen, (C₁-C₆)-alkyl, hydroxy-(C₁-C₆)-alkyl or phenyl; R⁵³ is hydrogen, (C₁-C₆)-alkyl or phenyl; and R⁵⁸ is (C₁-C₆)-alkyl or phenyl;

X is -OR²³⁰ or -SR²⁴⁰, wherein R²³⁰ and R²⁴⁰ are (C₁-C₆)-alkyl substituted by Q, phenyl substituted by Q, (C₁-C₆)-alkyl-SO₂-phenyl wherein the alkyl group is substituted by Q or (C₁-C₆)-alkyl-NH-SO₂-phenyl, wherein the alkyl group is substituted by Q;

Q is a tris-(C₁-C₆)-alkyl-ammonium group, a bis(C₁-C₆)-alkyl-benzyl-ammonium group, a methyl-morpholinium group or a methyl-pyrrolidinium group; and A⁻ is chloride, sulfate, hydrogensulfate, methylsulfate, ethylsulfate, phosphate, formate, acetate or lactate.

4. Hair dye composition according to claims 1 and/or 2, wherein in the general formula (I)

R is hydrogen or (C₁-C₆)-alkyl;

Z, T and R¹ are hydrogen;

Y is -NR⁵¹R⁵² or OR⁵³, wherein R⁵¹ and R⁵³ are hydrogen, R⁵² is (C₁-C₆)-alkyl, hydroxy-(C₁-C₆)-alkyl or phenyl;

X is -SO₂NR²⁷⁰R²⁸⁰, -CONR²⁹⁰R³⁰⁰, -SO₂OR³¹⁰, -C(O)OR³²⁰, wherein R²⁷⁰ and R²⁹⁰ are hydrogen or (C₁-C₆)-alkyl; R²⁸⁰, R³⁰⁰, R³¹⁰ and R³²⁰ are (C₁-C₆)-alkyl substituted by Q, hydroxy(C₁-C₆)-alkyl substituted in the alkyl group by Q or phenyl substituted by Q;

Q is a tris(C₁-C₆)-alkyl-ammonium group, a bis(C₁-C₆)-alkyl-benzyl-ammonium group, a methyl-morpholinium group or a methyl-pyrrolidinium group; and A⁻ is chloride, sulfate, hydrogensulfate, methylsulfate, ethylsulfate, phosphate, formate, acetate or lactate.

5. Hair dye composition according to claims 1 and/or 2, wherein in the general formula (I)

R is hydrogen or (C₁-C₆)-alkyl;

T and R¹ are hydrogen;

Z is -NR⁵¹R⁵² or -NHC(O)R⁵⁶, wherein R⁵¹ is hydrogen and R⁵² is hydrogen or

(C₁-C₆)-alkyl and R⁵⁶ is (C₁-C₆)-alkyl or phenyl;

Y is -NR⁵¹R⁵², wherein R⁵¹ is hydrogen, R⁵² is (C₁-C₆)-alkyl, hydroxy-(C₁-C₆)-alkyl or phenyl;

X is -OR²³⁰, -SO₂NR²⁷⁰R²⁸⁰ or -SO₂OR³¹⁰, wherein R²³⁰ and R³¹⁰ are (C₁-C₆)-alkyl substituted by Q, hydroxy(C₁-C₆)-alkyl substituted in the alkyl group by Q, phenyl substituted by Q; R²⁷⁰ is hydrogen, R²⁸⁰ is (C₁-C₆)-alkyl substituted by Q or hydroxy(C₁-C₆)-alkyl substituted in the alkyl group by Q;

Q is a tris(C₁-C₆)-alkyl-ammonium group, a bis(C₁-C₆)-alkyl-benzyl-ammonium group, a methyl-morpholinium group or a methyl-pyrrolidinium group; and

A⁻ is chloride, sulfate, hydrogensulfate, methylsulfate, ethylsulfate, phosphate, formate, acetate or lactate.

6. Hair dye composition according to claims 1 and/or 2, wherein in the general formula (I)

Y, T and R¹ are hydrogen;

R is hydrogen or (C₁-C₆)-alkyl;

Z is -NR⁵¹R⁵² or -NHC(O)R⁵⁶, wherein R⁵¹ is hydrogen and R⁵² is hydrogen or (C₁-C₆)-alkyl and R⁵⁶ is (C₁-C₆)-alkyl or phenyl;

X is -OR²³⁰, -SO₂NR²⁷⁰R²⁸⁰, -SO₂OR³¹⁰ or -NR²⁵⁰R²⁶⁰, wherein R²³⁰ and R³¹⁰ are

(C₁-C₆)-alkyl substituted by Q, hydroxy-(C₁-C₆)-alkyl substituted in the alkyl group by Q, or phenyl substituted by Q; R²⁷ is hydrogen, R²⁸ is (C₁-C₆)-alkyl substituted by Q or hydroxy-(C₁-C₆)-alkyl substituted in the alkyl group by Q; R²⁵ is hydrogen and R²⁶ is (C₁-C₆)-alkyl substituted by Q;

Q is a tris(C₁-C₆)-alkyl-ammonium group, a bis(C₁-C₆)-alkyl-benzyl-ammonium group, a methyl-morpholinium group or a methyl-pyrrolidinium group which is bonded to X; and

A⁻ is chloride, sulfate, hydrogensulfate, methylsulfate, ethylsulfate, phosphate, formate, acetate or lactate.

7. Hair dye composition according to claims 1 and/or 2, wherein in the general formula (I)

R is hydrogen or (C₁-C₆)-alkyl;

Z is -NR⁵¹R⁵² wherein R⁵¹ is hydrogen and R⁵² is hydrogen or (C₁-C₆)-alkyl;

Y is OR⁵³, wherein R⁵³ is hydrogen;

X is hydrogen,

R¹ is -NH₂ or -NH-alkyl;

T is alkyl substituted by Q or aryl substituted by -OR²³⁰; wherein R²³⁰ is (C₁-C₆)-alkyl substituted by Q, hydroxy(C₁-C₆)-alkyl substituted in the alkyl group by Q, -C(O)R⁶⁰⁰ or -SO₂R⁹⁰⁰ wherein R⁶⁰⁰ and R⁹⁰⁰ are (C₁-C₆)-alkyl substituted by Q or hydroxy(C₁-C₆)-alkyl substituted in the alkyl group by Q;

Q is a tris(C₁-C₆)-alkyl-ammonium group, a bis(C₁-C₆)-alkyl-benzyl-ammonium group, a methyl-morpholinium group or a methyl-pyrrolidinium group; and

A⁻ is chloride, sulfate, hydrogensulfate, methylsulfate, ethylsulfate, phosphate, formate, acetate or lactate.

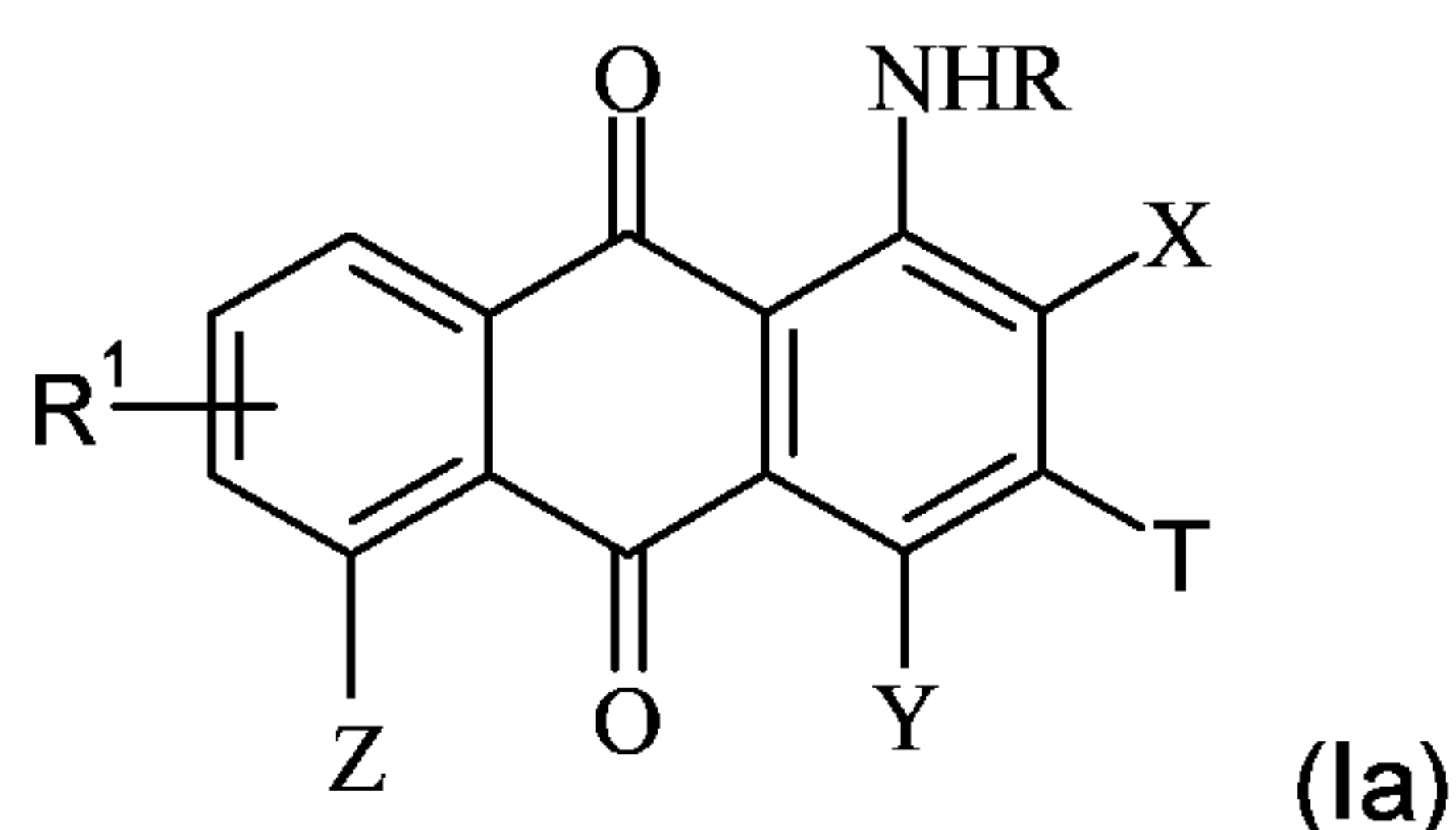
8. Hair dye composition according to one or more of claims 1 to 7, which comprises at least one oxidative dye precursor and/or at least one coupling compound.

9. Hair dye composition according to one or more of claims 1 to 8, which comprises an oxidizing agent.

10. Hair dye composition according to one or more of claims 1 to 9, which has a pH value in the range of 2 to 11.

11. Process for colouring hair characterized in that a hair dye composition according to one or more of claims 1 to 10 is applied onto hair, left for 1 to 45 minutes and then rinsed off from hair.

12. Dyestuff of the general formula (Ia)



wherein

R is hydrogen, alkyl, alkyl substituted by -OR², -SR³ or -NR⁵R⁴, hydroxyalkyl, polyhydroxyalkyl, cycloalkyl, aryl substituted by R¹⁰, R¹¹O-alkyl, -OR¹², -SR¹³, -NR¹⁴R¹⁵, -CONR¹⁵R¹⁶, -C(O)OR¹⁷, -SO₂-NR¹⁸R¹⁹, -SO₂OR²⁰, -C(O)R²¹ or -SO₂R²², -C(O)R⁶, -SO₂NR⁷R⁸ or -SO₂R⁹;

X is hydrogen, $-\text{OR}^{235}$, $-\text{SO}_2\text{NR}^{270}\text{R}^{280}$ or $-\text{SO}_2\text{OR}^{310}$;

Y is hydrogen, $-\text{NR}^{51}\text{R}^{52}$, $-\text{OR}^{53}$, $-\text{SR}^{54}$, $-\text{SO}_2\text{NHR}^{55}$, $-\text{NHC(O)R}^{56}$, $-\text{SO}_2\text{OR}^{57}$, $-\text{NHSO}_2\text{R}^{58}$, $-\text{SO}_2\text{R}^{59}$, $-\text{NHSO}_2\text{NR}^{60}\text{R}^{61}$, halogen or NO_2 ;

Z is hydrogen, $-\text{NR}^{51}\text{R}^{52}$, $-\text{OR}^{53}$, $-\text{SR}^{54}$, $-\text{SO}_2\text{NHR}^{55}$, $-\text{NHC(O)R}^{56}$, $-\text{SO}_2\text{OR}^{57}$,

5 $\text{NHSO}_2\text{R}^{58}$, $-\text{SO}_2\text{R}^{59}$, $-\text{NHSO}_2\text{NR}^{60}\text{R}^{61}$, halogen or NO_2 ;

T is hydrogen or aryl substituted by $-\text{OR}^{230}$;

R^1 is hydrogen, $-\text{OH}$, $-\text{NH}_2$, $-\text{NHalkyl}$ or NO_2 ;

R^{235} is aryl substituted by $-\text{SO}_2\text{NR}^{180}\text{R}^{190}$ or $-\text{SO}_2\text{R}^{220}$;

and Q, R^2 to R^{22} , R^{51} to R^{61} , R^{100} , R^{110} , R^{120} , R^{130} , R^{140} , R^{150} , R^{160} , R^{170} , R^{180} , R^{190} ,

10 R^{200} , R^{210} , R^{220} , R^{230} , R^{270} , R^{280} and R^{310} are defined as given in claim 1.

13. Dyestuff according to claim 12, where

Z is hydrogen or amino;

15 R^1 is hydrogen or hydroxy;

R is hydrogen;

Y is hydroxy or amino; and

X is $-\text{OR}^{235}$, wherein R^{235} is $(\text{C}_1\text{-C}_6)\text{-alkyl-NH-SO}_2\text{-phenyl}$, wherein the alkyl group is substituted by Q; and

20 T is hydrogen or aryl substituted by $-\text{OR}^{230}$, wherein R^{230} is $(\text{C}_1\text{-C}_6)\text{-alkyl}$ substituted by Q, hydroxy $(\text{C}_1\text{-C}_6)\text{-alkyl}$ substituted in the alkyl group by Q, $-\text{C(O)R}^{600}$ or $-\text{SO}_2\text{R}^{900}$, wherein R^{600} and R^{900} are $(\text{C}_1\text{-C}_6)\text{-alkyl}$ substituted by Q or hydroxy- $(\text{C}_1\text{-C}_6)\text{-alkyl}$ substituted in the alkyl group by Q.

