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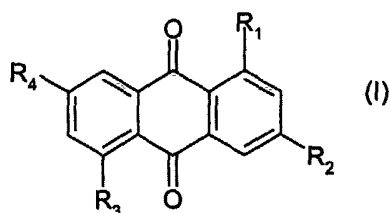
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(54) Title: ANTHRAQUINONE DYES



(I)

(57) Abstract: The present invention relates to a compound of formula (I) wherein R₁ and R₃ are each independently of the other -NHR₅, NHSO₂R₅, -NHCOR₅, -OR₆ or -SR₇, R₂ and R₄ are each independently of the other -OR₆ or -SR₇, with the proviso that not all of the substituents R₁ to R₄ are -SR₇, R₅ is hydrogen, alkyl, aryl, aralkyl or a group of formula -(C_nH_{2n}X)_m-H wherein X is -O-, -S-, -SO₂-, -NH-, -NR₈-, -CONH- or -CONR₈- and R₈ is alkyl or aryl, n is a number from 2 to 6 and m is a number from 1 to 10, R₆ is aryl or heteroaryl and R₇ is alkyl, aryl, heteroaryl or a group of formula -(C_nH_{2n}X)_m-H wherein X is -O-, -S-, -SO₂-, -NH-, NR₈-, COHN- or -CONR₈- and R₈

is alkyl or aryl, to a process for the preparation thereof and to the use thereof in a method of producing mass-coloured plastics or polymeric colour particles.

Anthraquinone dyes

The present invention relates to novel anthraquinone dyes, to a process for the preparation thereof and to the use thereof in a method of producing mass-coloured plastics or polymeric colour particles.

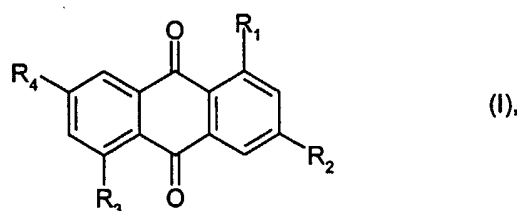
Dyes, especially dyes of the anthraquinone series, are known for mass-colouring plastics. For example there are described in US Patent 5 367 039 1,4,5,8-tetrasubstituted anthraquinones having (meth)acryloyl groups which can be copolymerised with vinyl monomers and are thus suitable for the production of coloured vinyl polymers.

The dyes used until now do not, however, meet the highest requirements in terms of light fastness and, especially, thermostability.

There is accordingly a need for novel thermostable dyes that produce colorations having a high tinctorial strength and exhibiting light fastness, especially high-temperature light fastness, and that have good all-round fastness properties.

It has now, surprisingly, been found that the dyes according to the invention substantially meet the above criteria.

The present invention accordingly relates to a compound of formula I



wherein

R_1 and R_3 are each independently of the other $-NHR_5$, $-NHSO_2R_5$, $-NHCOR_5$, $-OR_6$ or $-SR_7$,

R_2 and R_4 are each independently of the other $-OR_6$ or $-SR_7$,

with the proviso that not all of the substituents R_1 to R_4 are $-SR_7$,

R_5 is hydrogen, alkyl, aryl, aralkyl or a group of formula $-(C_nH_{2n}X)_m-H$ wherein X is $-O-$, $-S-$,

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-SO₂-, -NH-, -NR₈-, -CONH- or -CONR₈- and R₈ is alkyl or aryl, n is a number from 2 to 6 and m is a number from 1 to 10,

R₆ is aryl or heteroaryl and R₇ is alkyl, aryl, heteroaryl or a group of formula -(C_nH_{2n}X)_m-H wherein X is -O-, -S-, -SO₂-, -NH-, -NR₈-, -CONH- or -CONR₈- and R₈ is alkyl or aryl.

The substituents R₁ and R₃ may be identical or different; preferably, R₁ and R₃ are identical.

Likewise, R₂ and R₄ may be identical or different, but are preferably identical.

Any radical denoting alkyl may be a straight-chain or branched alkyl radical that may be substituted by one or more hydroxy groups, amino groups or halogen atoms.

Examples of alkyl groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, neopentyl, n-hexyl, n-heptyl, n-octyl, isooctyl, n-decyl and n-dodecyl.

Substituted alkyl groups include, for example, 2-hydroxyethyl, 2-hydroxypropyl, 4-hydroxybutyl, 2-aminoethyl, 2-aminopropyl, 4-aminobutyl, 2-chloroethyl, 2-bromoethyl and 4-chlorobutyl.

The aryl radicals designated R₅ to R₈ have preferably from 5 to 24, especially from 6 to 14, carbon atoms and may be substituted, for example, by hydroxy, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄hydroxyalkyl, halogen or by the radical -NH-CO-R wherein R is amino, C₁-C₄alkyl, unsubstituted phenyl or phenyl substituted by hydroxy, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄hydroxyalkyl or by halogen.

Examples of suitable aryl groups include phenyl, tolyl, mesityl, isityl, 2-hydroxyphenyl, 4-hydroxyphenyl, 2-chlorophenyl, 4-chlorophenyl, 2,6-dichlorophenyl, 2-aminophenyl, 3-aminophenyl, 4-aminophenyl, 4-methoxyphenyl, 4-ethoxyphenyl, 4-acetylaminophenyl, naphthyl and phenanthryl.

Aralkyl groups as R₅ have preferably from 6 to 30, especially from 7 to 12, carbon atoms and may be unsubstituted or substituted by one or more C₁-C₄alkyl groups, C₁-C₄alkoxy groups,

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halogen atoms or -NH-CO-R radicals wherein R is amino, C₁-C₄alkyl, unsubstituted phenyl or phenyl substituted by C₁-C₄alkyl, C₁-C₄alkoxy or by halogen.

Examples of suitable aralkyl groups include benzyl, 2-phenylethyl, tolylmethyl, mesitylmethyl and 4-chlorophenylmethyl.

Heteroaryl as R₆ or R₇ contains preferably 4 or 5 carbon atoms and one or two hetero atoms from the group O, S and N. It may be, for example, pyrrolyl, furyl, thiophenyl, oxazolyl, thiazolyl, pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolyl, purinyl or quinolyl.

In formula I, R₁ and R₃ are preferably -NHR₅ or -SR₇.

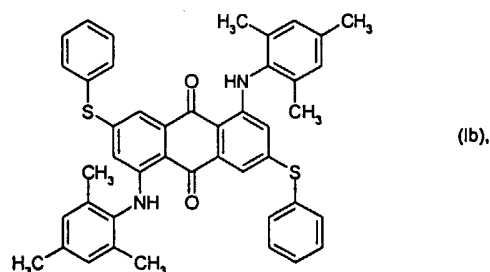
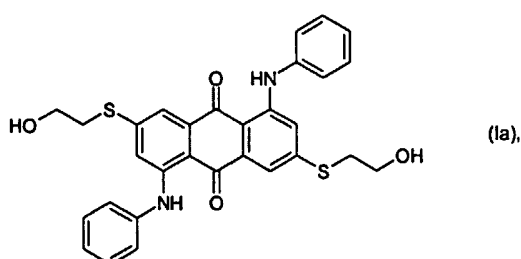
Preference is given to compounds of formula I wherein R₁ and R₃ are -NHR₅ or -SR₇ and R₅ and R₇ are aryl or hydroxyalkyl.

Special preference is given to compounds of formula I wherein R₁ and R₃ are -NHR₅ or -SR₇, R₅ is phenyl, mesityl or 2-hydroxyethyl and R₇ is phenyl.

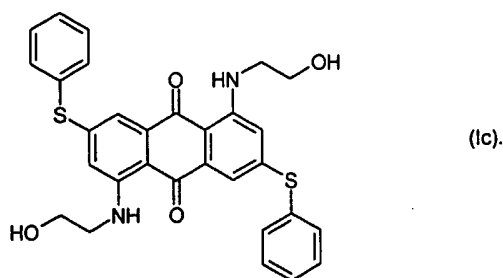
R₂ and R₄ in formula I are preferably -SR₇.

In especially preferred compounds of formula I, R₂ and R₄ are -SR₇ wherein R₇ is aryl or hydroxyalkyl, especially phenyl or 2-hydroxyethyl.

Special preference is given to compounds of formulae Ia - Ic



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The compounds of formula I can be prepared, for example, from 1,3,5,7-tetrabromoanthraquinone by reaction with suitable nucleophiles. In that reaction, advantageously in a first step the radicals R_1 and R_3 , which are preferably identical, are introduced into the reactive 1,5-positions. In a further nucleophilic substitution reaction, the remaining bromine atoms in the 3,7-positions are replaced by R_2 and R_4 , which are likewise preferably identical. When the radicals R_1 to R_4 are identical, the reaction can also be carried out in a single step.

1,3,5,7-Tetrabromoanthraquinone can, for example, be prepared in two steps from 1,5-diaminoanthraquinone. Bromination in aqueous hydrochloric acid yields 1,5-diamino-2,4,6,8-tetrabromoanthraquinone (R. Scholl, F. Eberle, W. Tritsch: Monatshefte für Chemie 32, 1055 (1911)), which can be converted, by diazotization and subsequent reduction, into 1,3,5,7-tetrabromoanthraquinone (H.Kopf, J. Fuchs, K.H. Eisenmann: Annalen der Chemie 585, 178 (1954); F. Ullmann, O. Eiser: Chemische Berichte 49, 2154 (1916)).

The invention relates also to a process for the preparation of a compound of formula I which comprises reacting 1,3,5,7-tetrabromoanthraquinone with a compound R_1 -H or with a mixture of the compounds R_1 -H and R_3 -H in a first reaction step, and then reacting the so-prepared intermediate with a compound R_2 -H or with a mixture of the compounds R_2 -H and R_4 -H, R_1 , R_2 , R_3 and R_4 being as defined hereinabove.

The compounds R_1 -H, R_2 -H, R_3 -H and R_4 -H are known or can be prepared in a manner known *per se*.

The present invention relates also to a method of producing mass-coloured plastics or polymeric colour particles which comprises mixing a high molecular weight organic material and a tinctorially effective amount of at least one compound of formula (I).

The colouring of the high molecular weight organic substances using the dye of formula (I) is carried out, for example, by using roll mills, mixing apparatus or grinding apparatus to admix such a dye with such substrates, the dye being dissolved or finely distributed in the high molecular weight material. The high molecular weight organic material with the admixed dye is then processed according to methods known *per se*, such as, for example, calendering, compression moulding, extrusion, coating, spinning, pouring or injection moulding, as a result of which the coloured material acquires its final form. Admixture of the dye can also be effected immediately prior to the actual processing step, for example by simultaneously continuously feeding, directly into the intake zone of an extruder, a solid, for example pulverulent, dye and a granulated or pulverulent high molecular weight organic material and, where appropriate, also other ingredients, such as additives, the constituents being mixed in just before being processed. Generally, however, preference is given to mixing the dye into the high molecular weight organic material beforehand, since more uniformly coloured substrates can be obtained.

In order to produce non-rigid shaped articles or to reduce their brittleness, it is frequently desirable to incorporate so-called plasticisers into the high molecular weight compounds prior to shaping. There may be used as plasticisers, for example, esters of phosphoric acid, phthalic acid or sebacic acid. In the method according to the invention, the plasticisers can be incorporated into the polymers before or after the incorporation of the colorant. It is also possible, in order to achieve different colour shades, to add to the high molecular weight organic substances, in addition to the dye of formula (I), also other pigments or other colorants in the desired amounts, optionally together with further additives, for example fillers or siccatives.

Preference is given to the colouring of thermoplastic plastics especially in the form of fibres. Preferred high molecular weight organic materials that can be coloured in accordance with the invention are very generally polymers having a dielectric constant ≥ 2.5 , especially polyester, polycarbonate (PC), polystyrene (PS), polymethyl methacrylate (PMMA), polyamide, polyethylene, polypropylene, styrene/acrylonitrile (SAN) or acrylonitrile/butadiene/styrene (ABS). Polyester and polyamide are especially preferred. More especially preferred are linear aromatic polyesters, which can be obtained by polycondensation of terephthalic acid and glycols, especially ethylene glycol, or condensation products of terephthalic acid and 1,4-bis(hydroxymethyl)cyclohexane, for example polyethylene

terephthalate (PET) or polybutylene terephthalate (PBT); also polycarbonates, e.g. those obtained from α,α -dimethyl-4,4-dihydroxy-diphenylmethane and phosgene, or polymers based on polyvinyl chloride and also on polyamide, for example polyamide 6 or polyamide 6.6.

When the compounds of formula (I) according to the invention contain at least two NH, OH or SH groups, mixing the dye with the monomers and incorporation thereof in the form of a comonomer directly into the polymer skeleton is possible, provided that the monomers contain reactive groups that react with the active hydrogen atoms of the NH, OH or SH groups. Examples of such monomers include epoxides (epoxy resins), isocyanates (polyurethanes) and carboxylic acid chlorides (polyamides, polyesters).

The invention accordingly relates also to a method of producing mass-coloured plastics or polymeric colour particles that comprises causing a mixture comprising at least one monomer that contains at least one NH-, OH- or SH-reactive group and is capable of polymerisation, polyaddition or polycondensation reactions to react with at least one compound of formula I containing at least two NH, OH or SH groups.

The present invention relates also to the use of compounds of formula I in the production of mass-coloured plastics or polymeric colour particles and to the plastics or polymeric colour particles coloured using the compounds of formula I.

The dyes according to the invention impart to the above-mentioned materials, especially polyester materials, level colour shades of high tinctorial strength that have good in-use fastness properties, especially very good high-temperature light fastness.

The dyes according to the invention can furthermore be used for coating applications of any kind.

The dyes according to the invention can also readily be used together with other dyes to produce blended shades.

The anthraquinone dyes of formula (I) according to the invention are furthermore suitable as colorants in the production of colour filters, especially for visible light in the range from 400 to 700 nm, for liquid crystal displays (LCDs) or charge combined devices (CCDs).

The production of colour filters by sequential application of a red, blue and green colorant to a suitable substrate, for example amorphous silicon, is described in GB-A 2 182 165. The colour filters can be coated, for example, using inks, especially printing inks, that comprise the anthraquinone dyes according to the invention, or can be produced, for example, by blending the anthraquinone dyes according to the invention with chemically, thermally or photolytically structurable high molecular weight material. The further production can be carried out, for example, analogously to EP-A 654 711 by application to a substrate, such as an LCD, followed by photo-structuring and development. Other documents that describe the production of colour filters include US-A 5 624 467, Displays 14/2, 115 (1993) and WO 98/45756.

The colour filters that are produced for liquid crystal displays (LCDs) using the anthraquinone dyes according to the invention are distinguished by high transmission of colour dots.

The invention relates also to the use of an anthraquinone dye according to the invention as a colorant in the production of colour filters.

The following Examples serve to illustrate the invention.

Example 1:

A. 1,5-Bis(2-hydroxyethylamino)-3,7-dibromoanthraquinone

90 g of 1,3,5,7-tetrabromoanthraquinone, 142.3 g of 2-aminoethanol, 18.6 g of sodium acetate and 0.52 g of copper(I) acetate are introduced into a laboratory reaction apparatus and stirred for 3 hours at 130°C. After cooling to room temperature (RT), the reaction mixture is taken up in ethanol and poured into water. After filtration and drying, 24 g (65%) of product are obtained.

B. 1,5-Bis(2-hydroxyethylamino)-3,7-bis(phenylmercapto)-anthraquinone

24 g of 1,5-bis(2-hydroxyethylamino)-3,7-dibromoanthraquinone are introduced at RT into 100 ml of dimethylformamide (DMF). After the addition of 16.3 g of sodium thiophenolate,

the mixture is heated to 120°C and maintained at that temperature for one hour. After cooling the mixture to RT, 100 ml of methanol are added thereto. The precipitate is filtered off, washed with a methanol/water mixture (1:1) and dried *in vacuo*.

Yield: 18.6 g (68.5%)

Example 2:

A. 1,5-Bis(phenylamino)-3,7-dibromoanthraquinone

20 g of 1,3,5,7-tetrabromoanthraquinone, 70 ml of aniline, 9.3 g of sodium acetate and 0.26 g of copper(I) acetate are introduced into a laboratory reaction apparatus and stirred for 2 hours at 150°C. After cooling the mixture to RT, the crude product is precipitated using ethanol, filtered off, washed and dried *in vacuo*.

Yield: 16.8 g (80%)

B. 1,5-Bis(phenylamino)-3,7-bis(2-hydroxyethylmercapto)-anthraquinone

16.8 g of 1,5-bis(phenylamino)-3,7-dibromoanthraquinone and 5.6 g of 2-hydroxyethylmercaptan are introduced at RT into 50 ml of DMF. After heating the mixture to 110°C, a solution of 8.16 g of potassium tert-butanolate in 90 ml of DMF is added. The mixture is stirred for 2 hours at 110°C. 500 ml of water are then added dropwise. The precipitate is filtered off, washed and dried *in vacuo*.

Yield: 11.4 g (70%)

Example 3:

A. 1,5-Bis(mesitylamino)-3,7-dibromoanthraquinone

37 g of 1,3,5,7-tetrabromoanthraquinone, 12.3 ml of mesidine, 17.3 g of sodium acetate and 0.5 g of copper(I) acetate are introduced into a laboratory reaction apparatus and stirred for 7 hours at 170°C. After cooling to RT, the crude product is precipitated by the addition of 1 litre of 2N HCl and recrystallised from ethanol. After filtration and drying 21 g (47%) of product are obtained.

B. 1,5-Bis(mesitylamino)-3,7-bis(phenylmercapto)-anthraquinone

16.5 g of 1,5-bis(mesitylamino)-3,7-dibromoanthraquinone are suspended at RT in 50 ml of DMF and heated to 120°C. After cooling to 50°C, a suspension of 8.5 g of sodium thiophenolate in 25 ml of DMF is added thereto. The mixture is then heated to 120°C again and stirred at that temperature for 1.5 hours. After cooling the mixture to 60°C, 100 ml of

methanol are added and the mixture is stirred overnight at RT. The precipitate is filtered off, washed with a methanol/water mixture (1:1) and dried *in vacuo*.

Yield: 11.2 g (62%)

Example 4:

1,3,5,7-Tetrakis(phenylmercapto)-anthraquinone

90 g of 1,3,5,7-tetrabromoanthraquinone and 50 g of sodium thiophenolate are suspended at 70°C in 150 ml of DMF in a laboratory reaction apparatus. The reaction mixture is stirred for 5 hours at 120°C. After cooling to RT, the precipitate is filtered off, washed with ethanol and dried *in vacuo*.

Yield: 22.6 g (73%)

II. Application Examples

II.1. Production of a colour filter for liquid crystal displays (LCDs)

In a 100 ml glass vessel containing 83.3 g of zirconium ceramic beads, 2.8 g of the anthraquinone dye according to Example 1, 0.28 g of Solsperse[®] 5000, 4.10 g of Disperbyk[®] 161 (dispersing agent, 30% solution of a high molecular weight block copolymer, containing groups having affinity for the pigment, in n-butyl acetate/1-methoxy-2-propyl acetate 1:6, BYK Chemie) and 14.62 g of 1-methoxy-2-propyl acetate (MPA) are stirred at 23°C for 10 minutes at 1000 revs/min. and for 180 minutes at 3000 revs/min. using a Dispermat. After the addition of 4.01 g of an acrylate polymer binder (35% solution in MPA), stirring is carried out at room temperature for 30 minutes at 3000 revs/min.. Following removal of the beads, the dispersion is diluted with an equal weight of MPA.

Using a spin-coating apparatus, a glass substrate (Corning type 1737-F) is coated with the resulting dispersion and centrifuged for 30 seconds at 1000 revs/min.. The layer is dried on a hot plate for 2 minutes at 100°C and for 5 minutes at 200°C. The resulting layer thickness is 0.4 µm.

The following anthraquinone dyes (Table 1), which are likewise suitable for mass-colouring plastics, can be prepared analogously to Example 1:

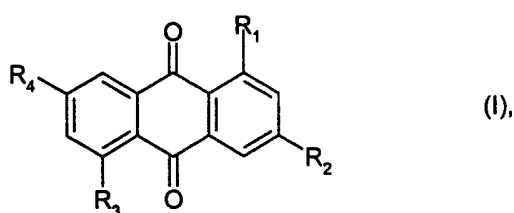
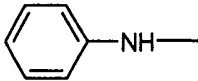
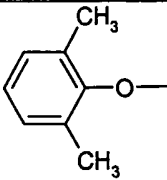
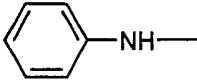
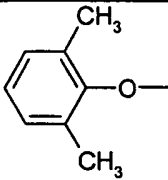
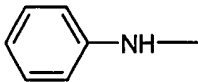
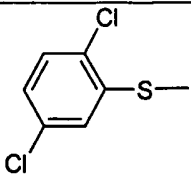
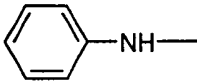
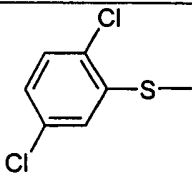
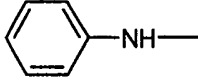
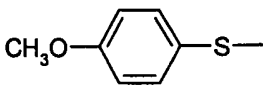
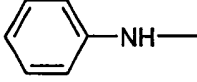
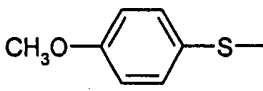
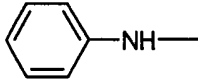
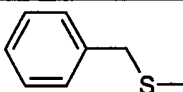
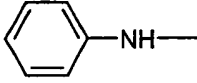
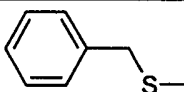
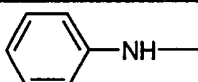
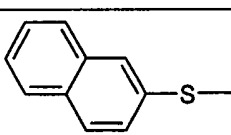
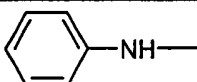
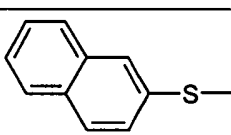
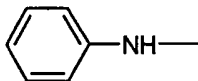
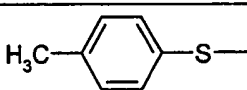
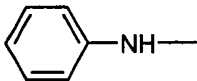
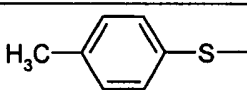
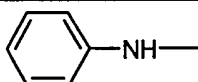
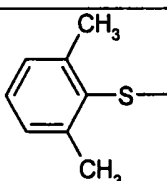
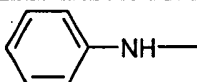
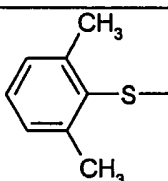
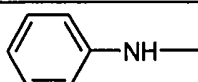
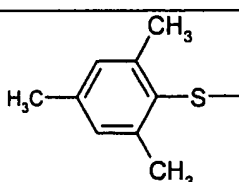
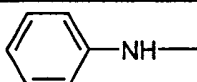
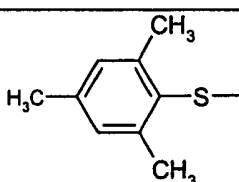
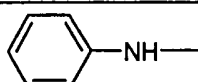
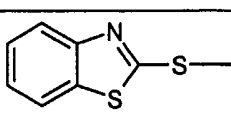
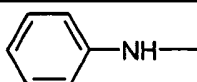
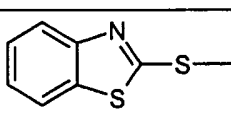
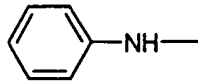
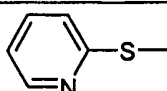
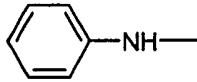
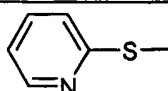
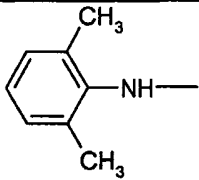
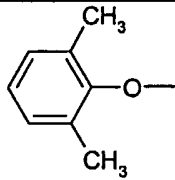
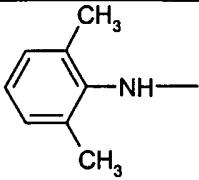
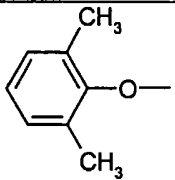
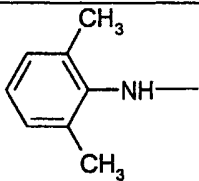
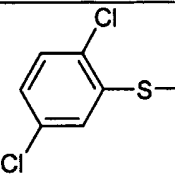
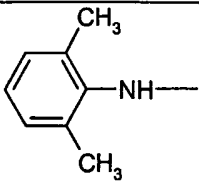
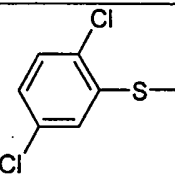
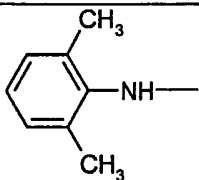
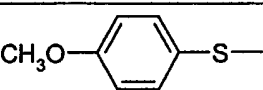
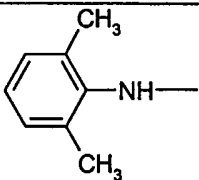
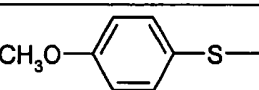
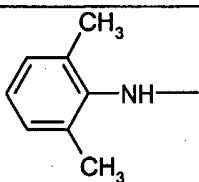
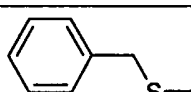
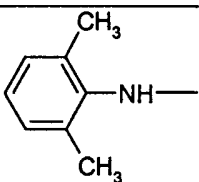
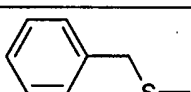
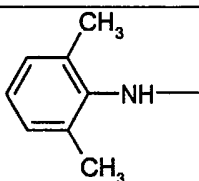
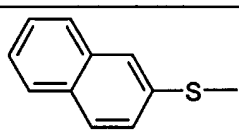
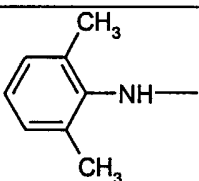
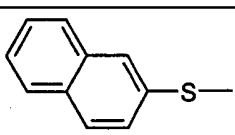
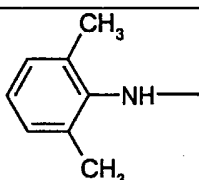
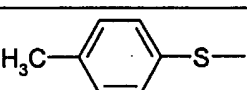
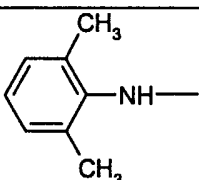
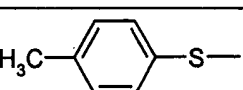
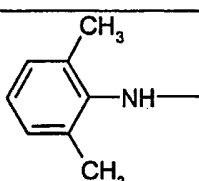
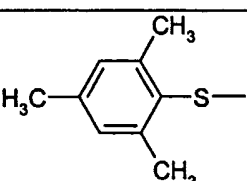
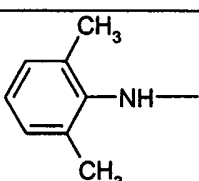
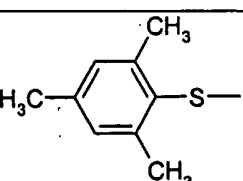
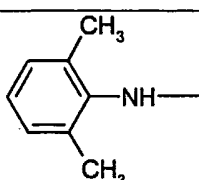
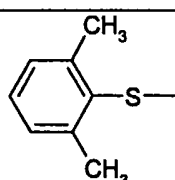
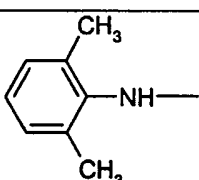
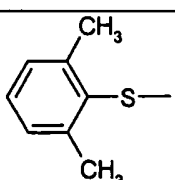


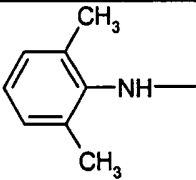
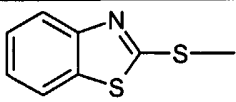
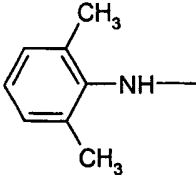
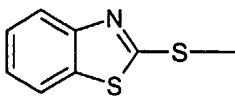
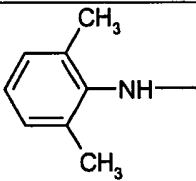
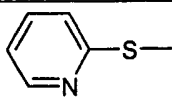
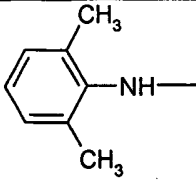
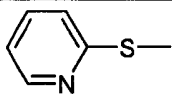
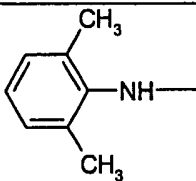
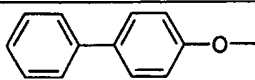
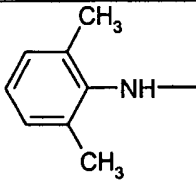
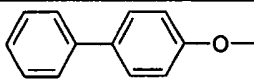
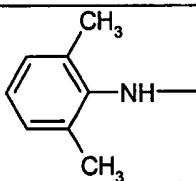
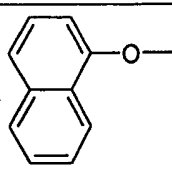
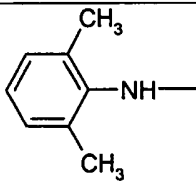
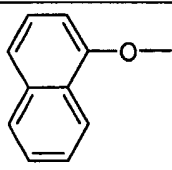
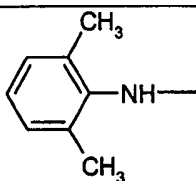
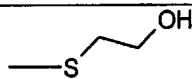
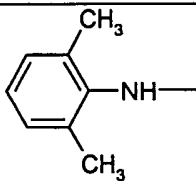
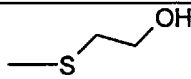
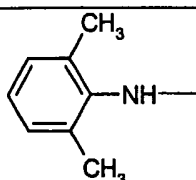
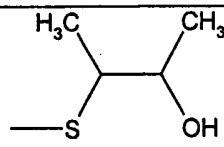
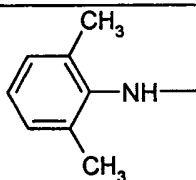
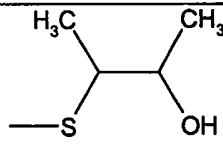
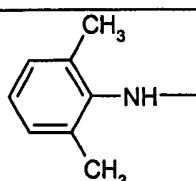
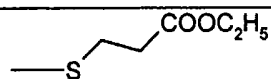
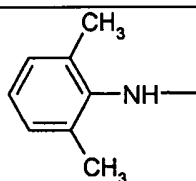
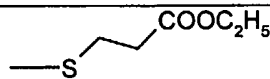
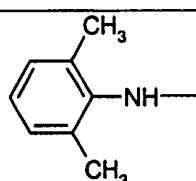
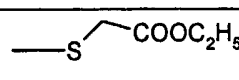
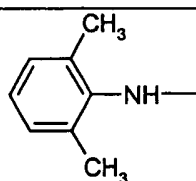
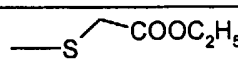
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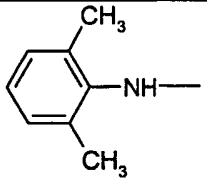

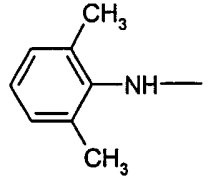
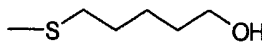
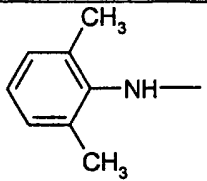
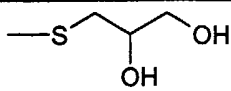
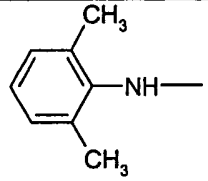
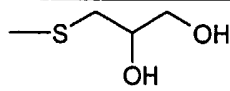
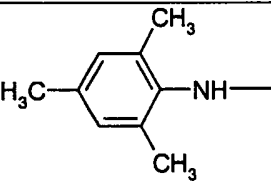
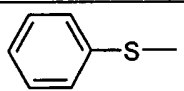
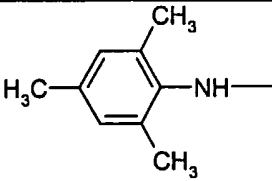
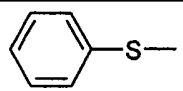
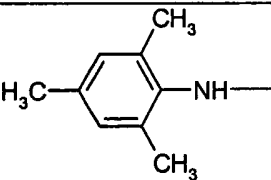
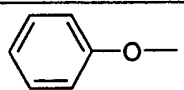
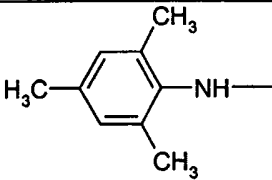
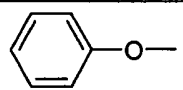
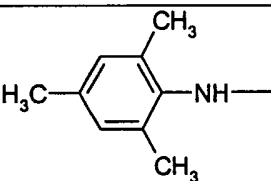
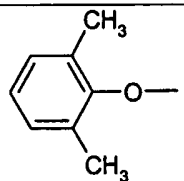
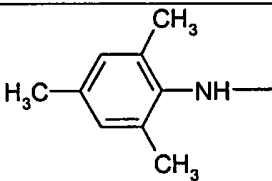
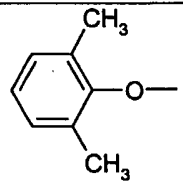
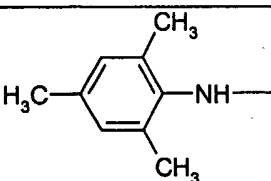
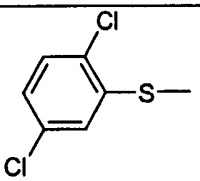
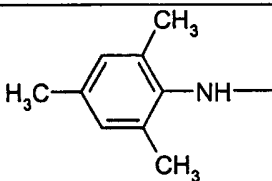
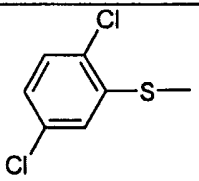
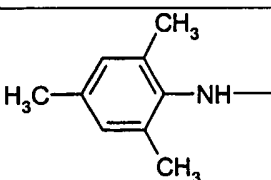
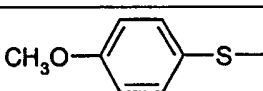
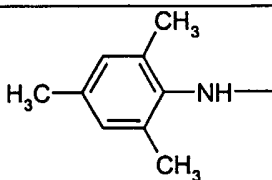
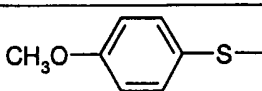
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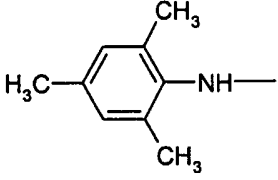
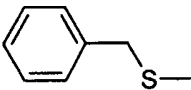
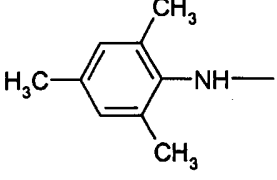
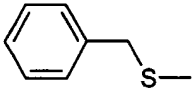
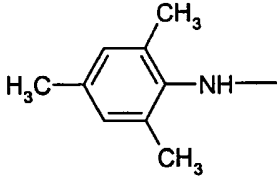
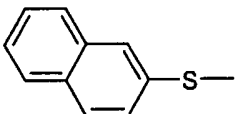
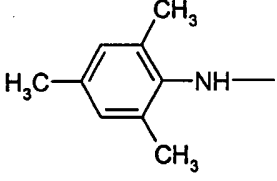
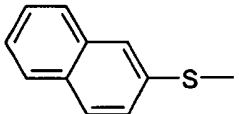
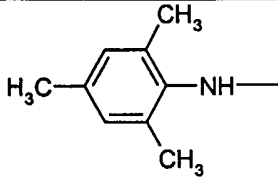
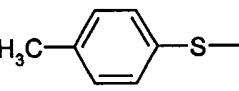
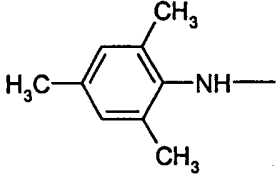
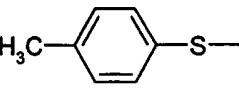
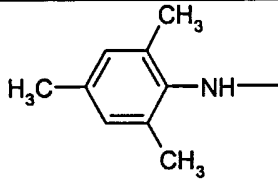
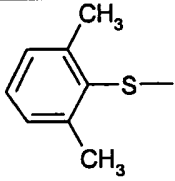
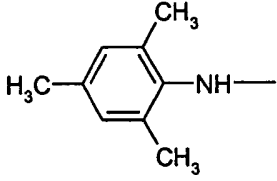
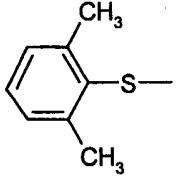
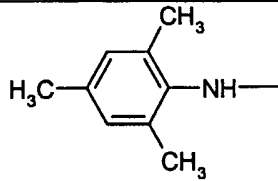
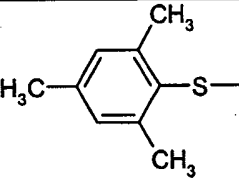
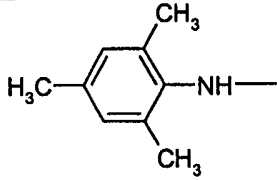
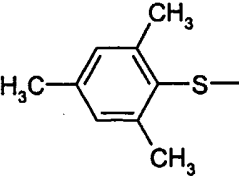
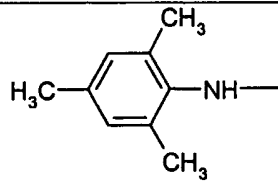
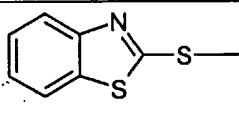
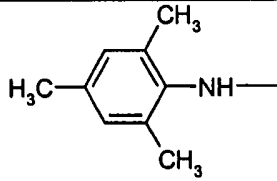
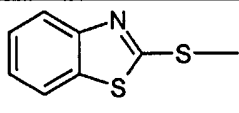
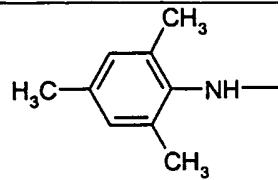
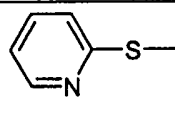
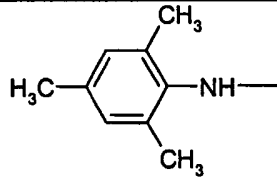
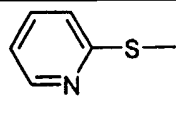
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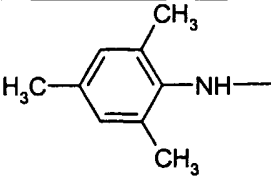
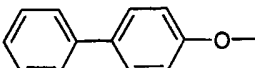
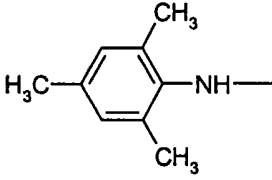
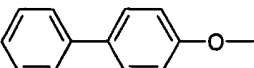
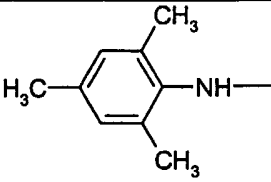
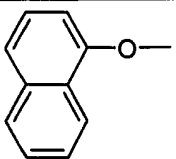
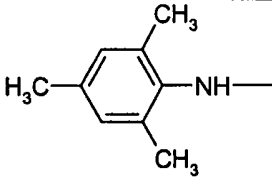
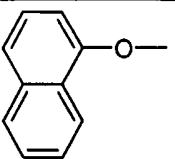
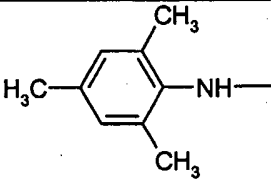
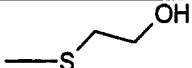
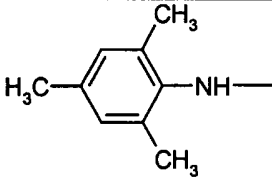
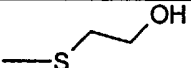
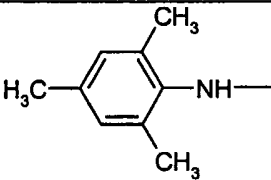
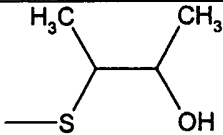
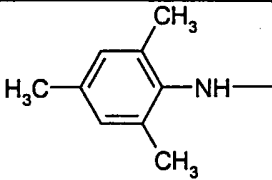
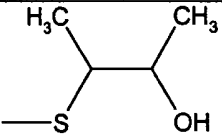
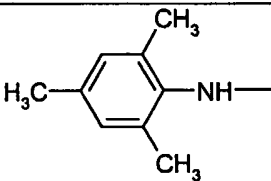
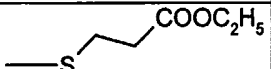
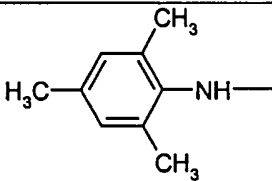
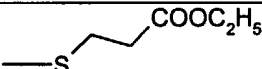
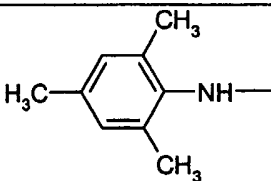
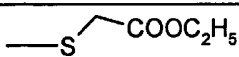
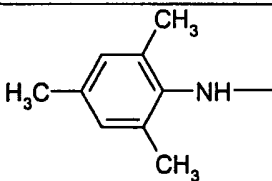
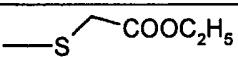
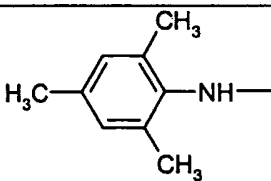
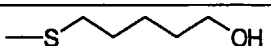
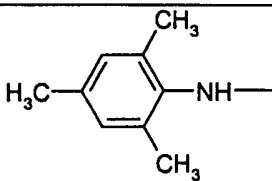
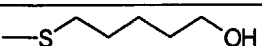
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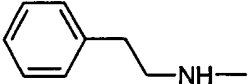
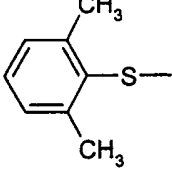
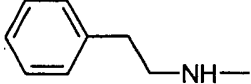
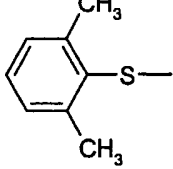
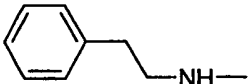
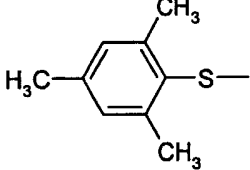
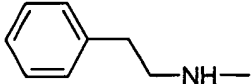
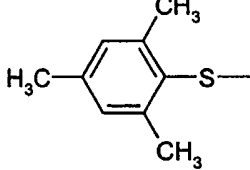
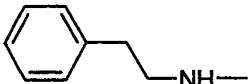
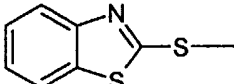
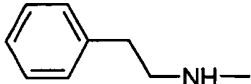
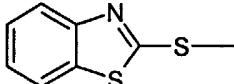
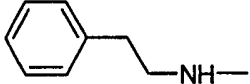
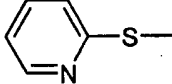
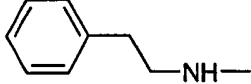
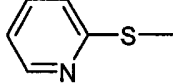
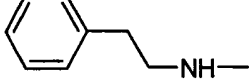
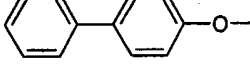
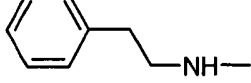
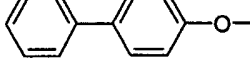
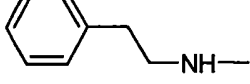
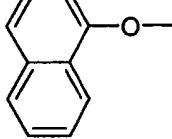
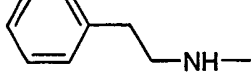
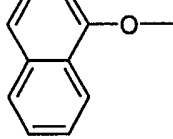
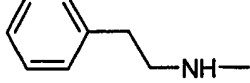
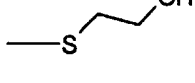
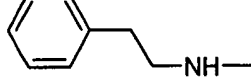
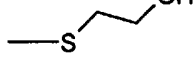
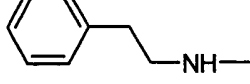
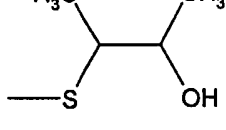
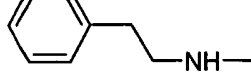
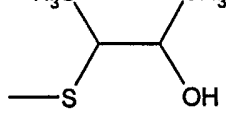
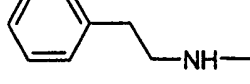
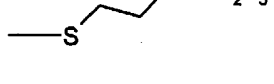
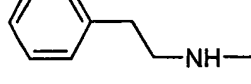
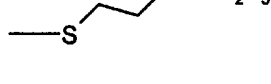
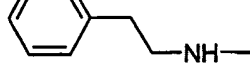
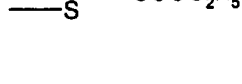
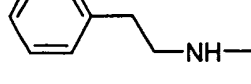

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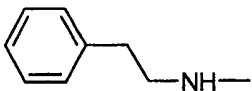

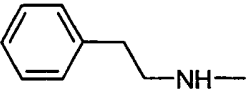
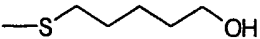
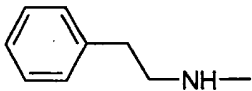
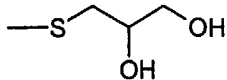
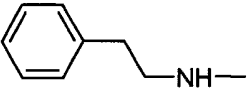
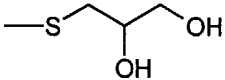
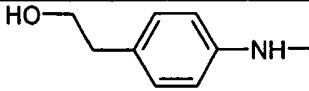
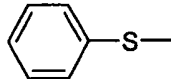
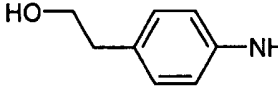
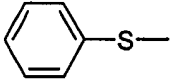
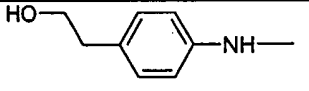
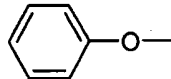
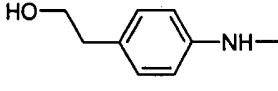
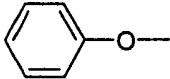
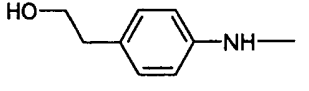
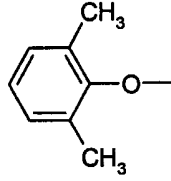
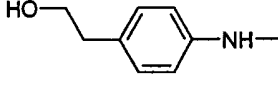
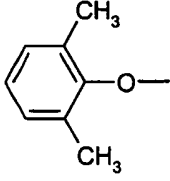
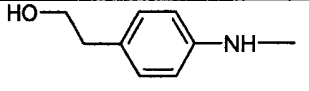
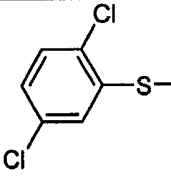
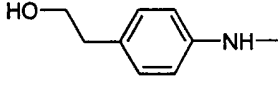
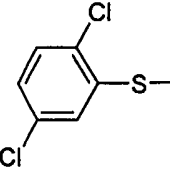
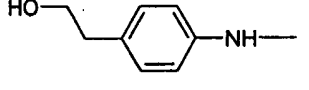
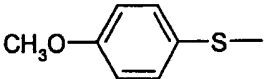
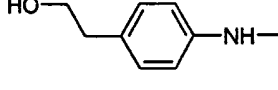
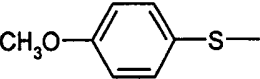
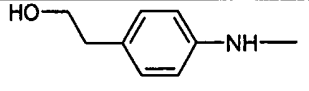
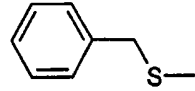
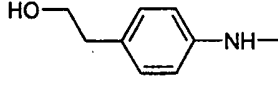
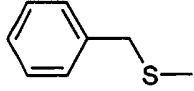
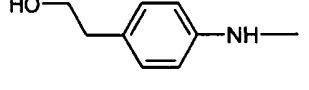
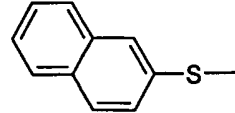
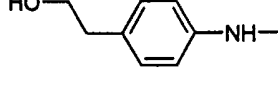
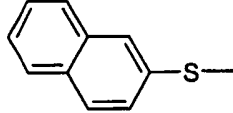
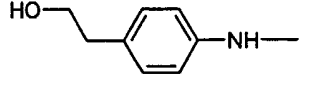
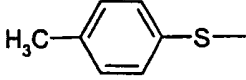
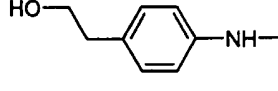
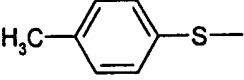
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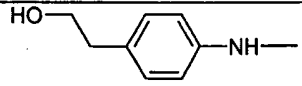
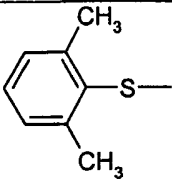
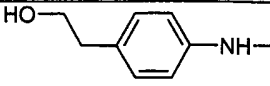
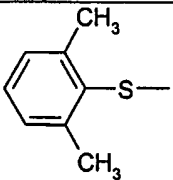
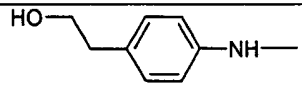
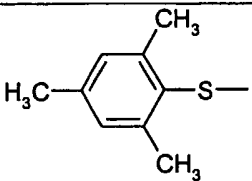
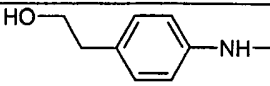
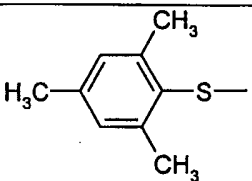
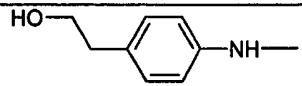
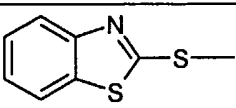
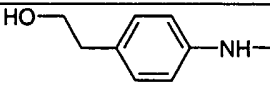
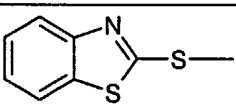
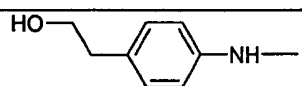
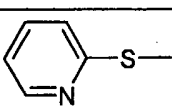
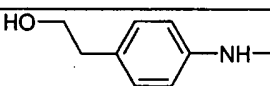
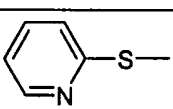
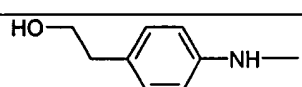
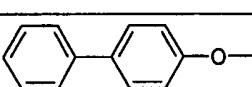
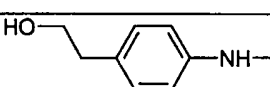
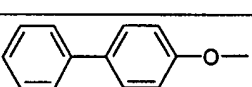
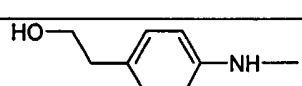
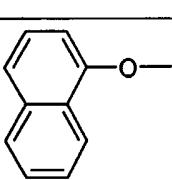
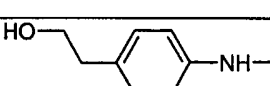
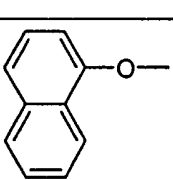
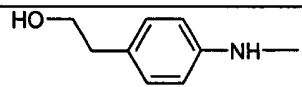
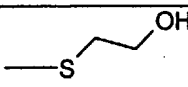
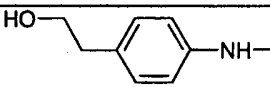
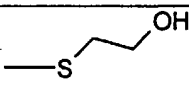
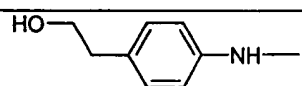
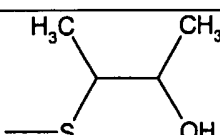
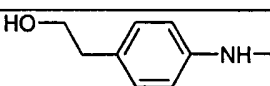
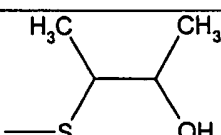
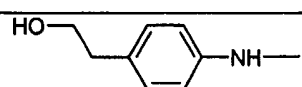
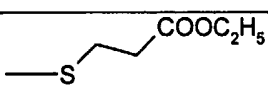
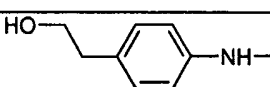
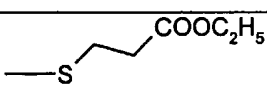
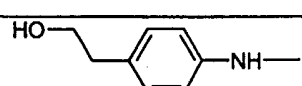
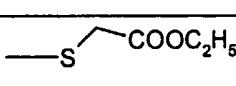
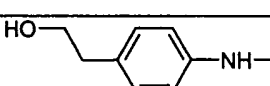
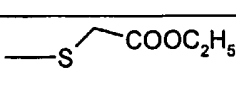
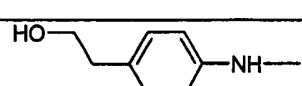
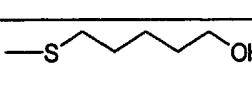
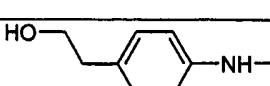
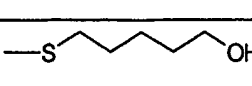
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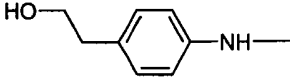
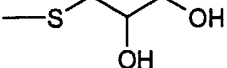
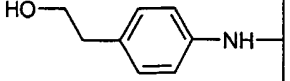
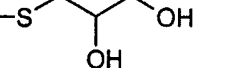
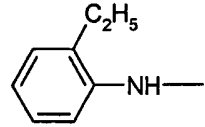
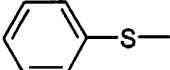
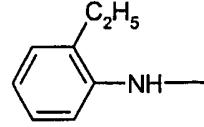
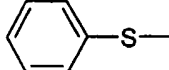
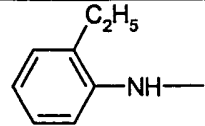
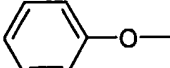
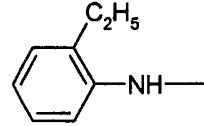
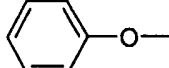
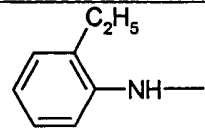
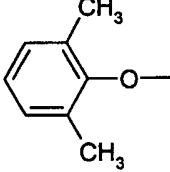
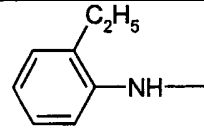
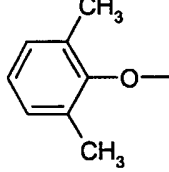
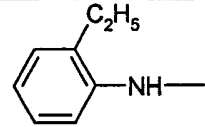
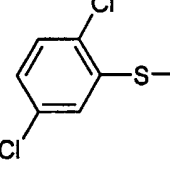
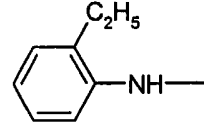
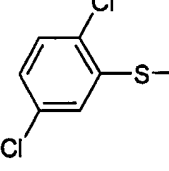
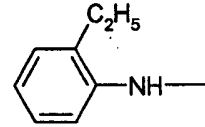
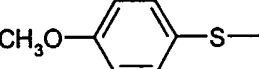
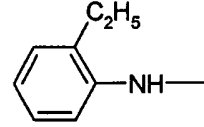
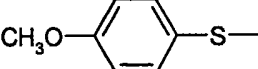
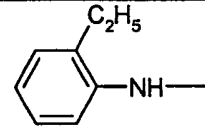
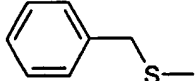
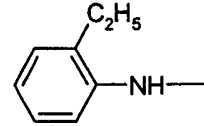
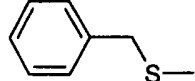
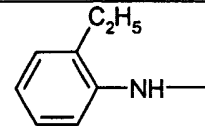
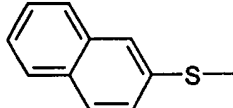
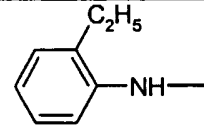
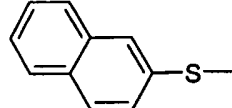
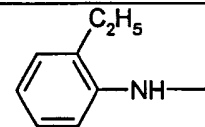

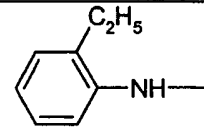

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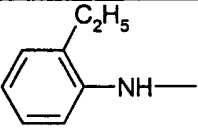
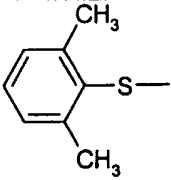
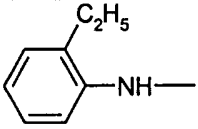
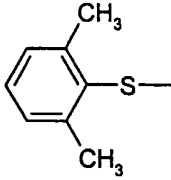
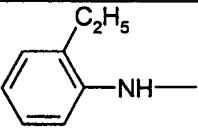
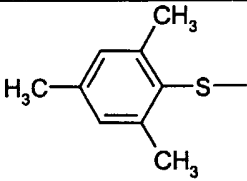
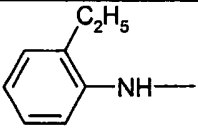
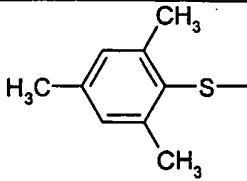
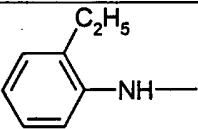
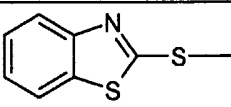
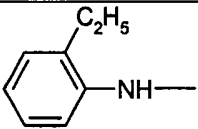
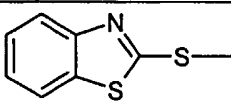
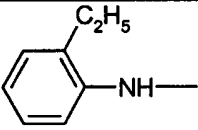
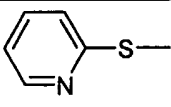
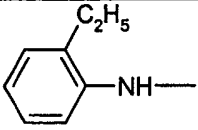
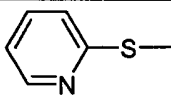
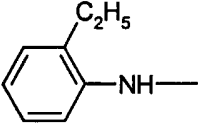
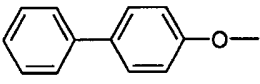
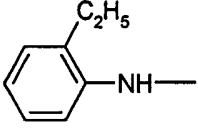
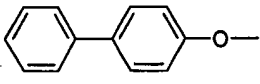
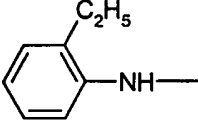
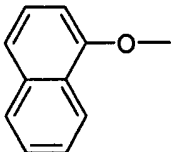
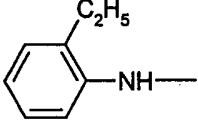
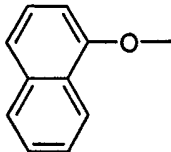
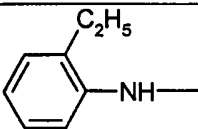
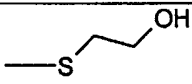
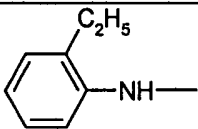
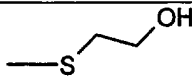
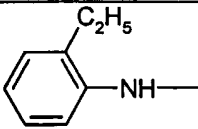
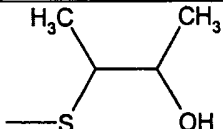
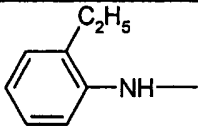
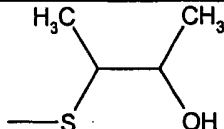
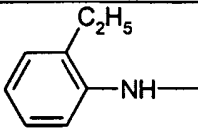
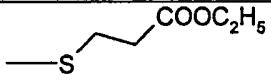
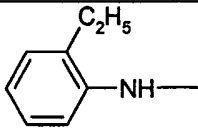
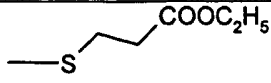
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R ₁	R ₂	R ₃	R ₄
			
			
			
			
			
			
			
			
			
			

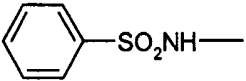
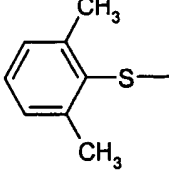
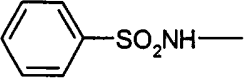
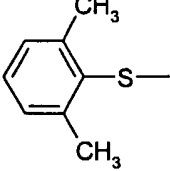
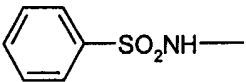
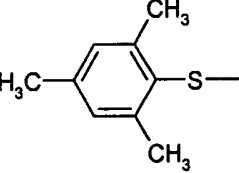
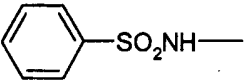
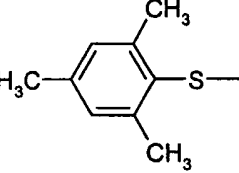
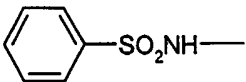
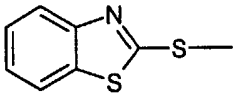
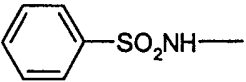
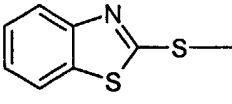
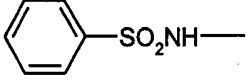
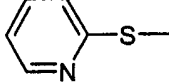
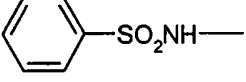
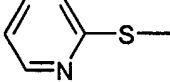
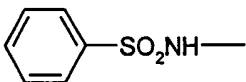
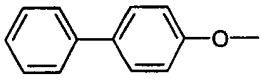
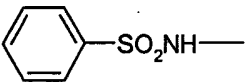
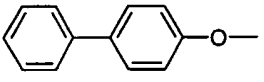
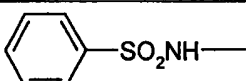
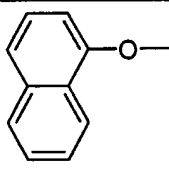
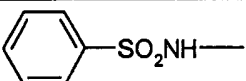
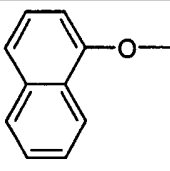
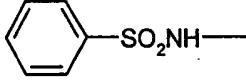
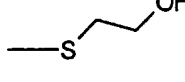
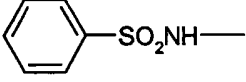
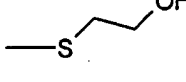
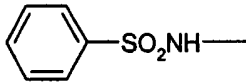
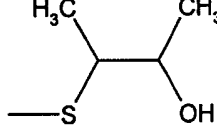
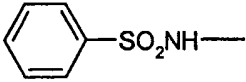
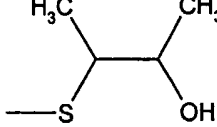
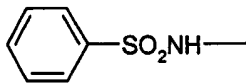
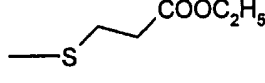
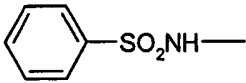
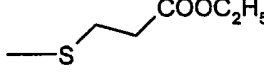
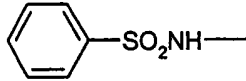
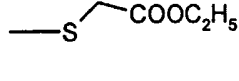
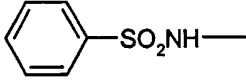
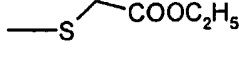
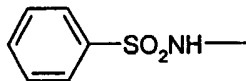
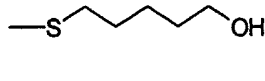
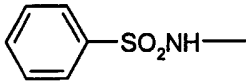
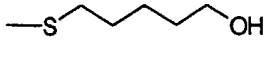
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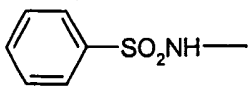
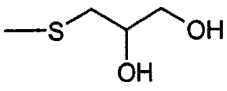
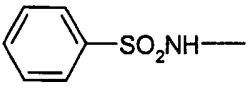
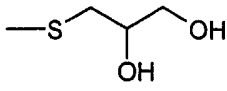
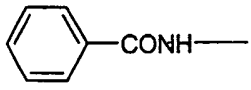
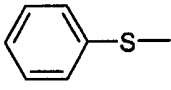
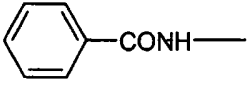
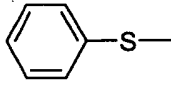
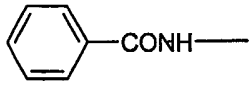
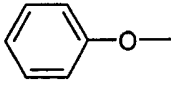
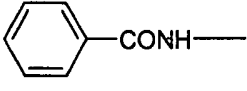
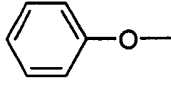
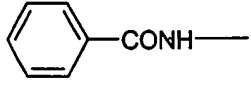
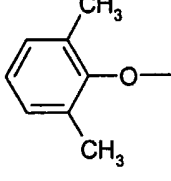
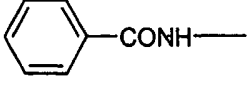
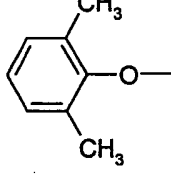
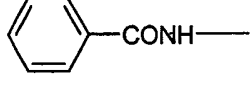
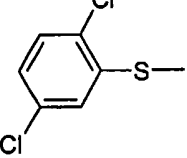
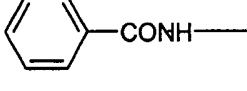
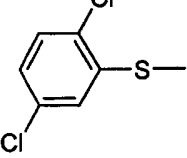
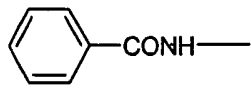
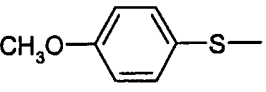
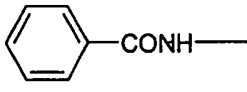
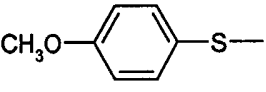
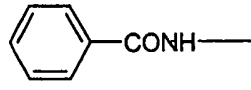
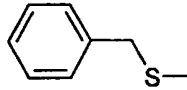
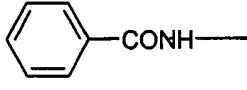
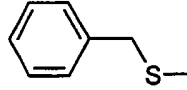
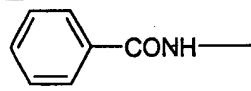
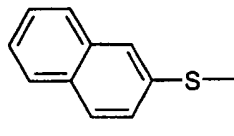
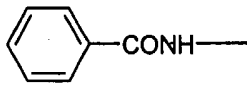
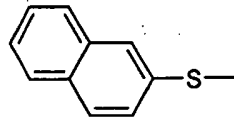
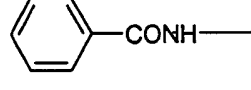
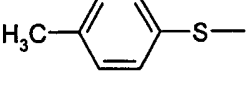
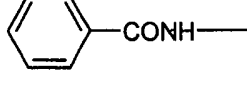
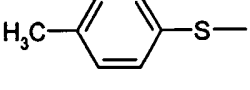
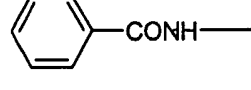
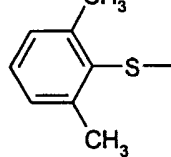
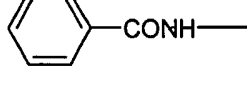
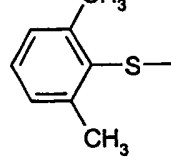
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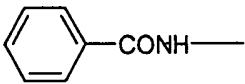
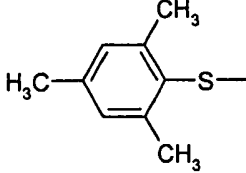
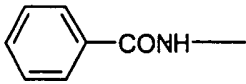
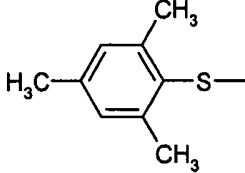
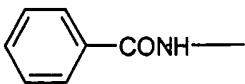
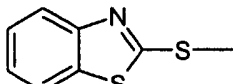
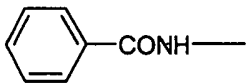
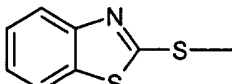
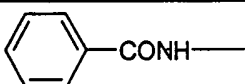
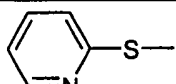
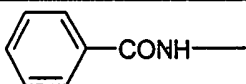
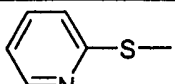
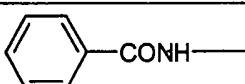
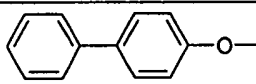
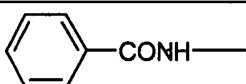
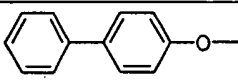
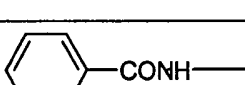
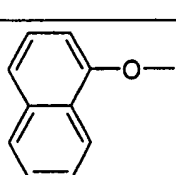
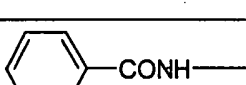
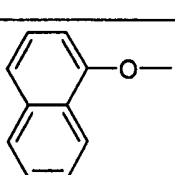
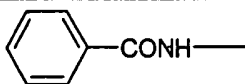
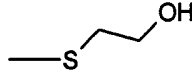
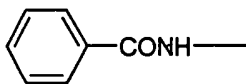
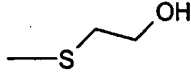
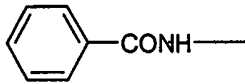
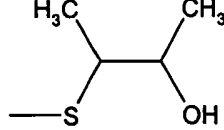
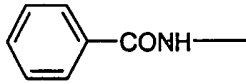
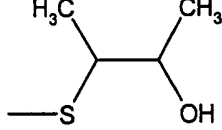
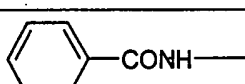
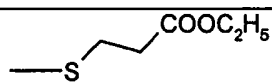
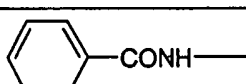
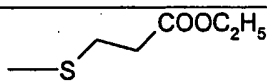
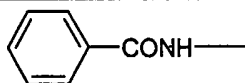
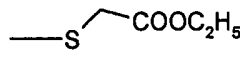
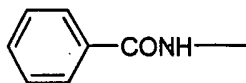
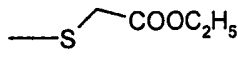
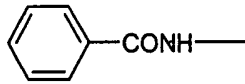
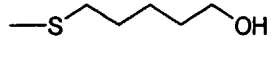
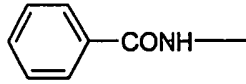
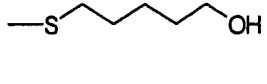
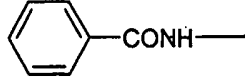
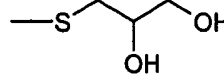
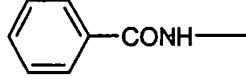
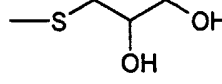

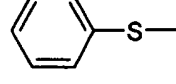

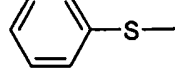
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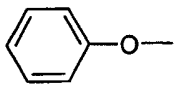
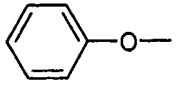
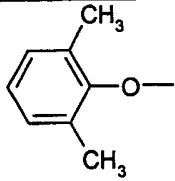
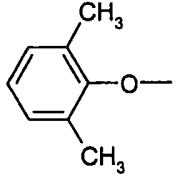
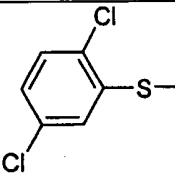
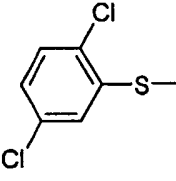
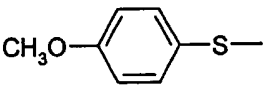
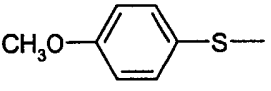
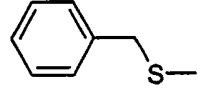
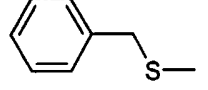
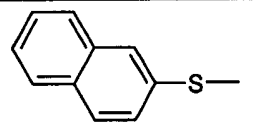
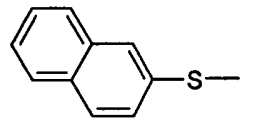
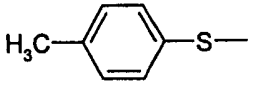
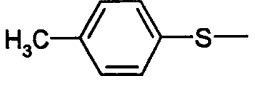
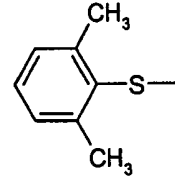
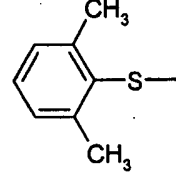
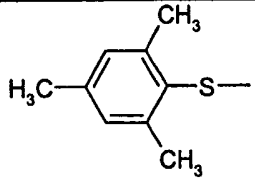
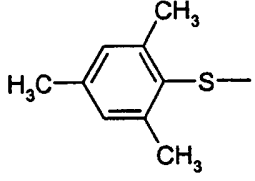
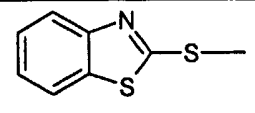
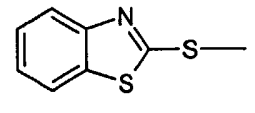
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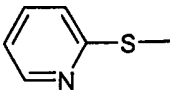
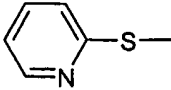
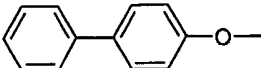
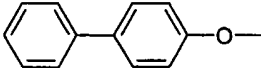
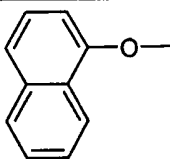
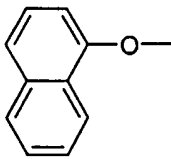
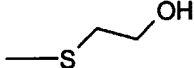
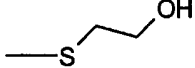
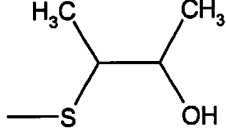
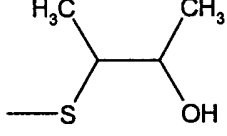
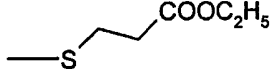
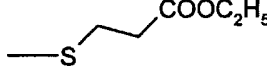
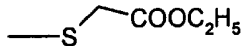
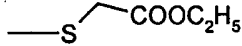
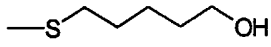
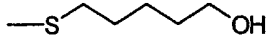
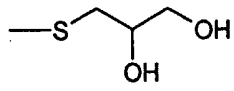
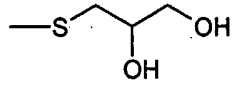
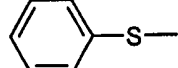
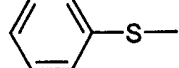
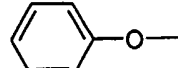
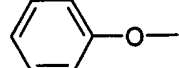
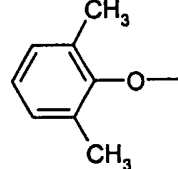
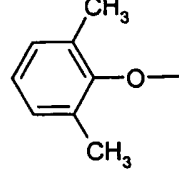
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—NHCH ₂ CH ₂ OH		—NHCH ₂ CH ₂ OH	

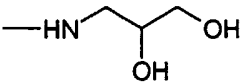
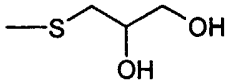
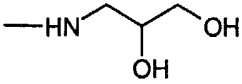
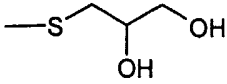
R ₁	R ₂	R ₃	R ₄

R ₁	R ₂	R ₃	R ₄

R ₁	R ₂	R ₃	R ₄

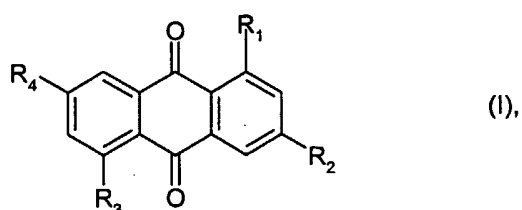
R ₁	R ₂	R ₃	R ₄

R ₁	R ₂	R ₃	R ₄

R ₁	R ₂	R ₃	R ₄
			

What is claimed is :

1. A compound of formula I



wherein

R_1 and R_3 are each independently of the other $-NHR_5$, $-NHSO_2R_5$, $-NHCOR_5$, $-OR_6$ or $-SR_7$,
 R_2 and R_4 are each independently of the other $-OR_6$ or $-SR_7$,
 with the proviso that not all of the substituents R_1 to R_4 are $-SR_7$,
 R_5 is hydrogen, alkyl, aryl, aralkyl or a group of formula $-(C_nH_{2n}X)_m-H$ wherein X is $-O-$, $-S-$, $-SO_2-$, $-NH-$, $-NR_8-$, $-CONH-$ or $-CONR_8-$ and R_8 is alkyl or aryl, n is a number from 2 to 6 and m is a number from 1 to 10,
 R_6 is aryl or heteroaryl and R_7 is alkyl, aryl, heteroaryl or a group of formula $-(C_nH_{2n}X)_m-H$ wherein X is $-O-$, $-S-$, $-SO_2-$, $-NH-$, $-NR_8-$, $-CONH-$ or $-CONR_8-$ and R_8 is alkyl or aryl.

2. A compound of formula I according to claim 1 wherein R_1 and R_3 are $-NHR_5$ or $-SR_7$ and R_5 and R_7 are as defined in claim 1.

3. A compound of formula I according to claim 1 wherein R_1 and R_3 are $-NHR_5$ or $-SR_7$ and R_5 and R_7 are aryl or hydroxyalkyl.

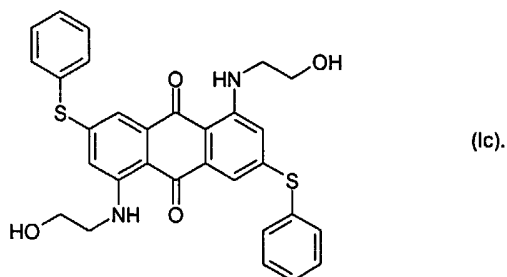
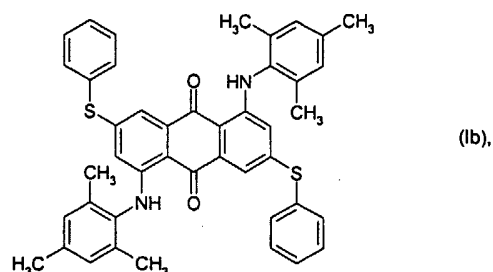
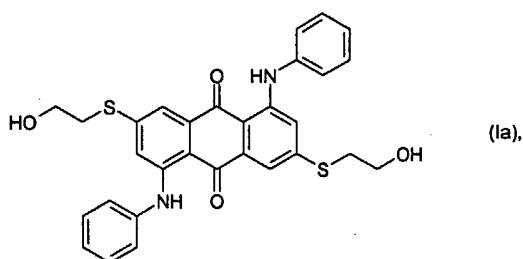
4. A compound of formula I according to claim 3 wherein R_5 is phenyl, mesityl or 2-hydroxyethyl and R_7 is phenyl.

5. A compound of formula I according to either claim 1 or claim 2 wherein R_2 and R_4 are $-SR_7$ and R_7 is as defined in claim 1.

6. A compound of formula I according to claim 5 wherein R_7 is aryl or hydroxyalkyl.

7. A compound of formula I according to claim 6 wherein R_7 is phenyl or 2-hydroxyethyl.

8. A compound of formula I according to claim 1 according to any one of formulae Ia to Ic



9. A process for the preparation of a compound of formula I according to claim 1 which comprises reacting 1,3,5,7-tetrabromoanthraquinone with a compound R_1 -H or with a mixture of the compounds R_1 -H and R_3 -H in a first reaction step, and then reacting the so-prepared intermediate with a compound R_2 -H or with a mixture of the compounds R_2 -H and R_4 -H, R_1 , R_2 , R_3 and R_4 being as defined in claim 1.

10. Use of a compound of formula I according to any one of claims 1 to 8 in the production of mass-coloured plastics or polymeric colour particles.

11. A method of producing mass-coloured plastics or polymeric colour particles that comprises mixing a high molecular weight organic material and a tinctorially effective amount of at least one compound of formula I.

12. A method of producing mass-coloured plastics or polymeric colour particles that comprises causing a mixture comprising at least one monomer that contains at least one NH-, OH- or SH-reactive group and is capable of polymerisation, polyaddition or

polycondensation reactions to react with at least one compound of formula I according to claim 1 that contains at least two NH, OH or SH groups.

13. Plastics or polymeric colour particles coloured in accordance with a method according to either claim 11 or claim 12.

14. Use of an anthraquinone dye according to claim 1 as a colorant in the production of colour filters.

INTERNATIONAL SEARCH REPORT

 Internat Application No
 PCT/EP 03/02615

A. CLASSIFICATION OF SUBJECT MATTER

 IPC 7 C09B1/54 C09B1/58 C09B1/56 G02B5/22 C08K5/37
 //C08K5/04,C08K5/16,G02F1/1335,

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B G02B C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	PATENT ABSTRACTS OF JAPAN vol. 012, no. 148 (C-493), 7 May 1988 (1988-05-07) -& JP 62 265355 A (MITSUBISHI CHEM IND LTD), 18 November 1987 (1987-11-18) abstract; table 2 ---	1-14
A	EP 1 127 922 A (CIBA SC HOLDING AG) 29 August 2001 (2001-08-29) claims; examples ---	1-14
A	GB 1 402 704 A (BAYER AG) 13 August 1975 (1975-08-13) page 1, line 5 -page 2, line 31; examples 17-22 --- -/--	1-14



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * & * document member of the same patent family

Date of the actual completion of the international search

25 June 2003

Date of mailing of the international search report

04/07/2003

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INTERNATIONAL SEARCH REPORT

Internatⁿ Application No
PCT/EP 03/02615

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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