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(72) Inventeurs/Inventors:
LUETHGE, THOMAS, DE;
ZOCH, HEINZ, DE;
MCINTOSH, RALPH, DE;
BERGEMANN, KLAUS, DE;
FANGHAENEL, EGON, DE;
KNACKFUSS, BERND, DE

(73) Propriétaire/Owner:
EVONIK DEGUSSA GMBH, DE

(74) Agent: MARKS & CLERK

(54) Titre : MATERIAU RENFERMANT DU CARBONE
(54) Title: CARBON-CONTAINING MATERIAL

(57) Abrégé/Abstract:

A carbon-containing material with organic groups obtainable by reacting carbon-containing material with organic compounds of the general formula I R^1-N=N-R^2 (I). The carbon-containing material with organic groups is produced by reacting the carbon-containing material with an organic compound of the general formula I. The material may be used as a filler, reinforcing filler, UV stabiliser, conductive carbon black or pigment.

Abstract

A carbon-containing material with organic groups obtainable by reacting carbon-containing material with organic compounds of the general formula I

$$R^1\text{-}N{=}N\text{-}R^2 \qquad \text{(I)}.$$

The carbon-containing material with organic groups is produced by reacting the carbon-containing material with an organic compound of the general formula I.

The material may be used as a filler, reinforcing filler, UV stabiliser, conductive carbon black or pigment.

Carbon-containing material

The invention relates to a carbon-containing material, to a process for the production thereof and to the use thereof.

EP 0569503 discloses a process for surface-modifying carbon-containing material with aromatic groups by electrochemical reduction of a diazonium salt.

It is furthermore known to provide carbon-containing material with organic groups by coupling the organic groups with the carbon-containing material by diazotisation (WO 96/18688).

It is further known to provide carbon-containing material with organic groups by binding the organic groups to the carbon-containing material by means of reactions with free-radical formers (Ohkita K., Tsubokawa N., Saitoh E., Carbon 16 (1978) 41); DE 10012784.3) or by cycloaddition reactions (DE 10012783.5).

It is known to react carbon-containing material with aliphatic compounds which have azo groups (JP11315220 A; Tsubokawa N., Kawatsura K., Shirai Y., Int. Conf. Mater. Proc. 11 (1997) 537; Tsubokawa N., Yanadori K., Sone Y., Nippon Gomu Kyokaishi 63 (1990) 268). The bond is formed between the compounds containing azo groups and the carbon-containing material with elimination of nitrogen and formation of free-radical species which may act as starter functions for further reactions (grafting).

It is likewise known to modify carbon-containing material by reaction with sulfuric acid or SO_3 (US 3519452; JP 2001-254033).

Known processes have the following disadvantages:

- The nonionic, organic nitrites also used for diazotisation in addition to the toxic, oxidising substance sodium nitrite, are toxic and highly combustible. Residues of the nitrites (counterions, alkyl residues) remain as unbound contaminants in the carbon-containing material.

- It is necessary to use nitrite in an acidic medium in order to carry out diazotisation, which may result in the formation of toxic nitrogen oxides.

- Free-radical formers are thermally or photochemically labile, explosive and may bring about difficult to control chain reactions.

- Synthesis and purification of the corresponding precursors of the free-radical formers in some cases involve substances which are toxic or constitute an odour nuisance and are thus costly with regard to the production process, transport, use and ultimate disposal.

- The nitrogen extrusion which occurs in cyclisation reactions with nitrogen heterocycles may result in sudden, explosive expansions in volume or increases in pressure, which substantially complicate reaction control.

- The reaction of carbon-containing material with compounds which have azo groups and form free-radicals with nitrogen extrusion may likewise result in sudden, explosive expansions in volume or increases in pressure, or alternatively in chain reactions which are difficult to control thermally and so complicate reaction control.

- Particularly stable, corrosion- and temperature-resistant materials are required for the reaction of carbon-containing material with sulfuric acid or fuming sulfuric acid, unwanted and hazardous oxidations may occur as secondary reactions and, due to the neutralisation which is required, waste water with elevated salinity may arise after the reaction, it being possible for a proportion of the salts arising to remain behind as contaminants on the carbon-containing material, which may lead to applicational disadvantages.

The object of the invention is to provide a carbon-containing material with organic groups, wherein

- modification of the carbon-containing material is variable in such a manner that the functional groups may be close to and/or very distant from the surface,

- modification of the carbon-containing material proceeds without upstream reactions, such as activation with starters,

- the reactions with the modifying agents according to the invention proceed purely thermally and no further catalysts (for example Lewis acids) or other activation variants, such as for example photochemical processes, are required,

- due to the chemical properties of the modifying agents according to the invention, no disruptive secondary reactions or difficult to control chain reactions can occur,

- the resultant carbon-containing material is not contaminated by acids, salts and the like, such that no purification of the carbon-containing material is necessary,
- the carbon-containing material does not need to be dried with an elevated energy input,
- no toxic waste gases arise during the modification,
- no or only small quantities of readily removable solvents are necessary.

The present invention provides a carbon-containing material with organic groups, which is characterised in that it is obtainable by reacting carbon-containing material with organic compounds of the general formula I,

$$R^1\text{-}N{=}N\text{-}R^2 \qquad (I)$$

wherein R^1 and R^2 may be identical or different and are aryl groups which are unsubstituted or substituted with acceptor or donor substituents.

The groups R^1 and R^2 may be part of a cyclic system.

The acceptor or donor substituents may be hydrophilic or hydrophobic. The structural unit of the general formula I may be present in the organic group once or in multiple instances.

Acceptor substituents may be $-COOR^3$, $-CO-R^3$, $-CN$, $-SCN$, $-NCS$, $-NCO$, $-SO_2R^3$ or $-SO_2OR^3$, with R^3 = H, alkyl, aryl or functionalised alkyl or aryl, such as for example ωcarboxyalkyl, $HSO_3-C_xH_y-$, $H_2N-C_xH_y-$ or $H_2N-SO_2-C_xH_y-$ ($x = 1-20$, $y = 2-40$).

Donor substituents may be alkyl or aryl groups, OR^4, $N(R^4)_2$, SR^4, $-S-S-R^4$ or $P(R^4)_2$, wherein R^4 is identical or different and consists of H, alkyl, aryl, or functionalised alkyl or aryl.

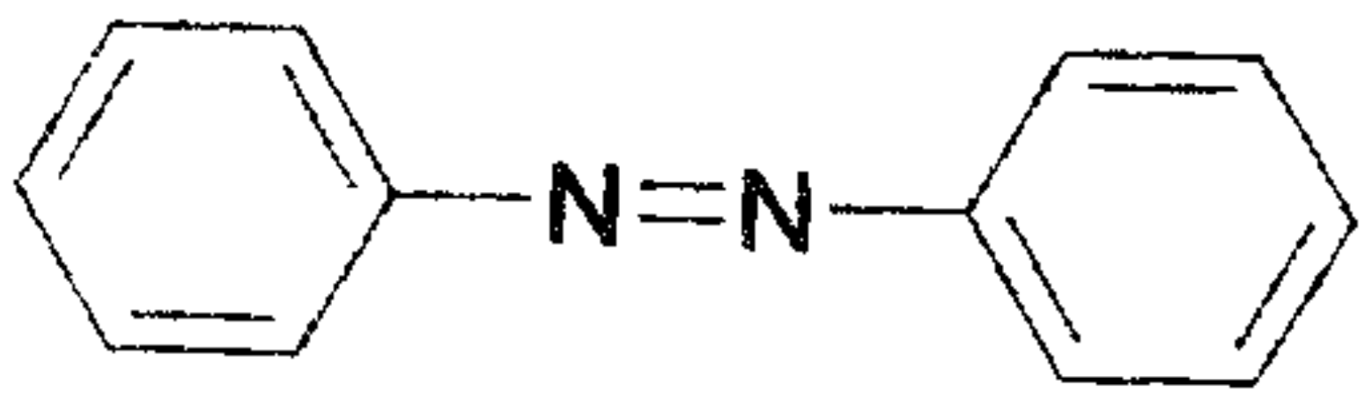
The organic groups R^1 and R^2 may:

- be substituted or unsubstituted, aromatic or heteroaromatic, branched or unbranched,
- contain an aliphatic group, for example residues from among alkanes, alkenes, alcohols, ethers, aldehydes, ketones, carboxylic acids, carboxylic acid esters, carboxylic acid amides, hydrocarbons, sulfonic acids, trialkylammonium, trialkylphosphonium or dialkylsulfonium,
- contain a cyclic compound, for example alicyclic hydrocarbons, such as for example cycloalkyls or cycloalkenyls, heterocyclic compounds, such as for example pyrrolidinyl, pyrrolinyl, piperidinyl or morpholinyl, aryl groups, such as for example phenyl, naphthyl or anthracenyl and heteroaryl groups, such as for example imidazolyl, pyrazolyl, pyridinyl, thienyl, thiazolyl, furyl or indolyl,
- be substituted by further functional groups,
- be a chromophoric group or a dye or parts thereof,

- bear suitable reactive compounds, such as for example triarylammonium, triarylphosphonium, diarylsulfonium or aryliodonium.

The substituents of the carbon-containing material with organic groups according to the invention may here be tailored to potential areas of application, as the identified reaction principle permits, for example, the introduction of both hydrophilic and lipophilic substituents. The substituents may also be ionic, polymeric or reactive in further reactions. Various properties of the carbon-containing material which are of great applicational significance may purposefully be modified by means of the substituents. For example, the hydrophilicity of the carbon-containing material may be increased to such an extent that the carbon-containing material forms stable dispersions in aqueous media without the use of a wetting agent.

Suitable azo compounds according to the invention may be: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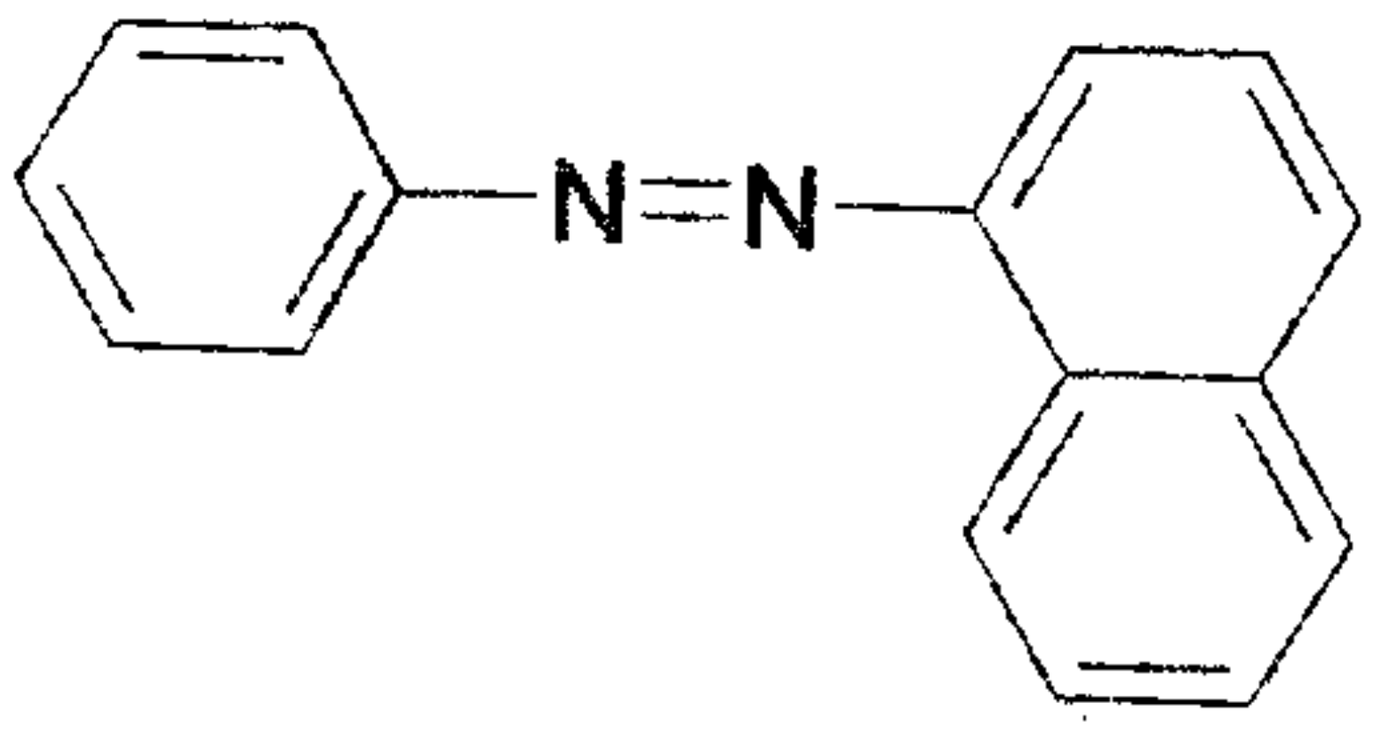
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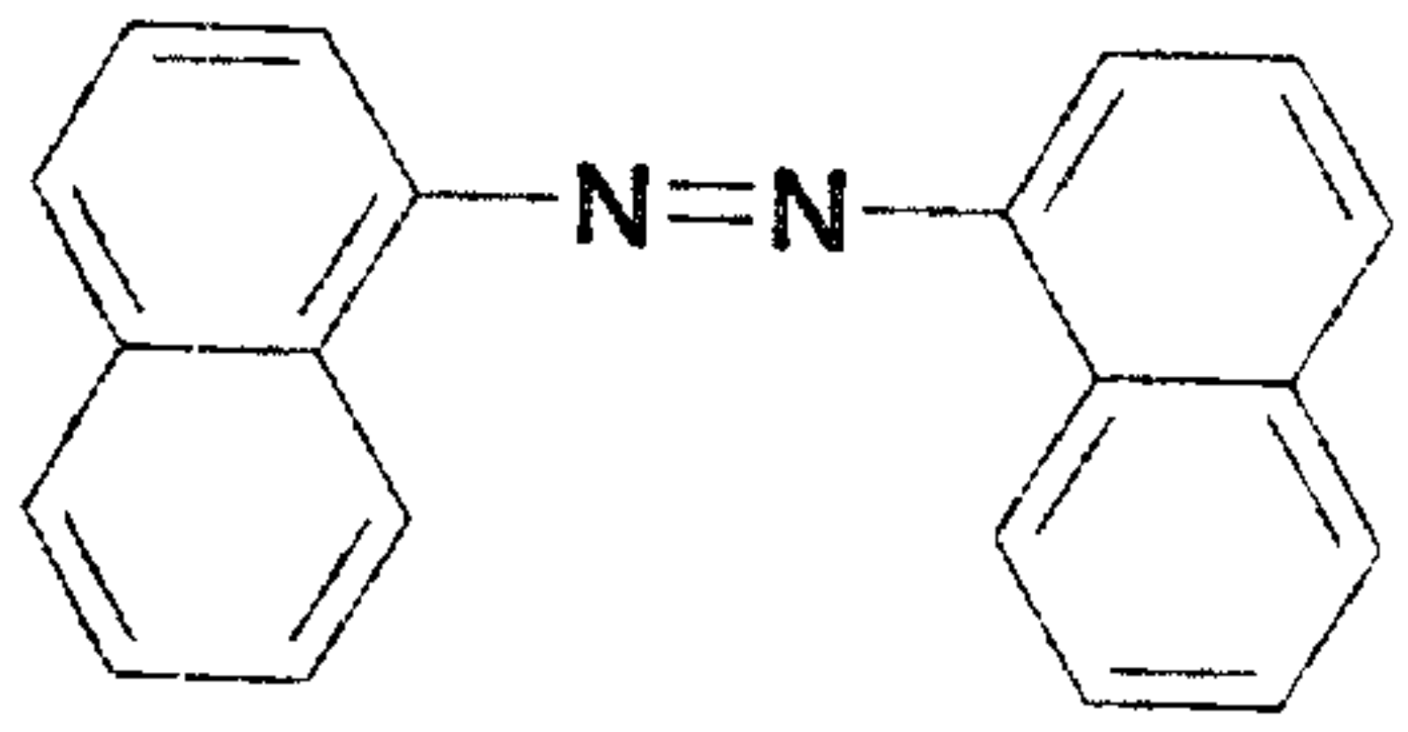
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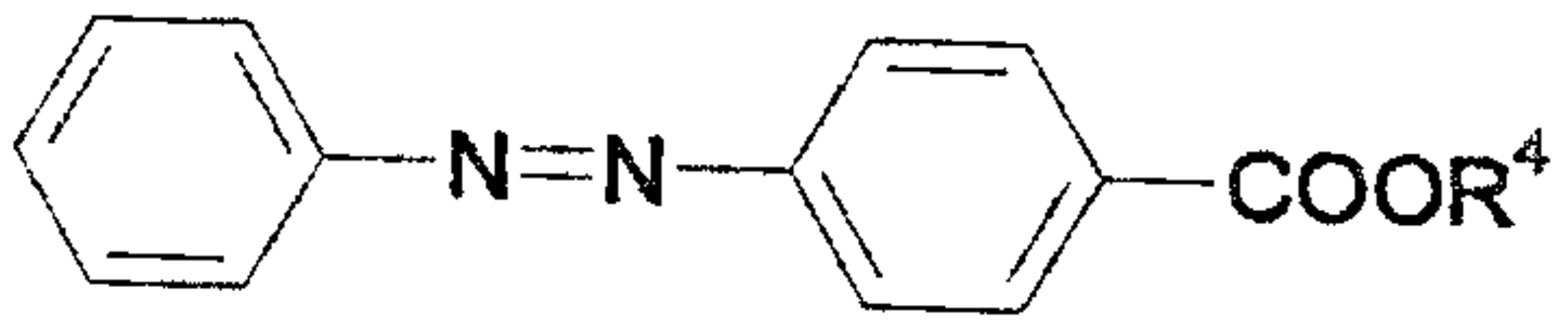
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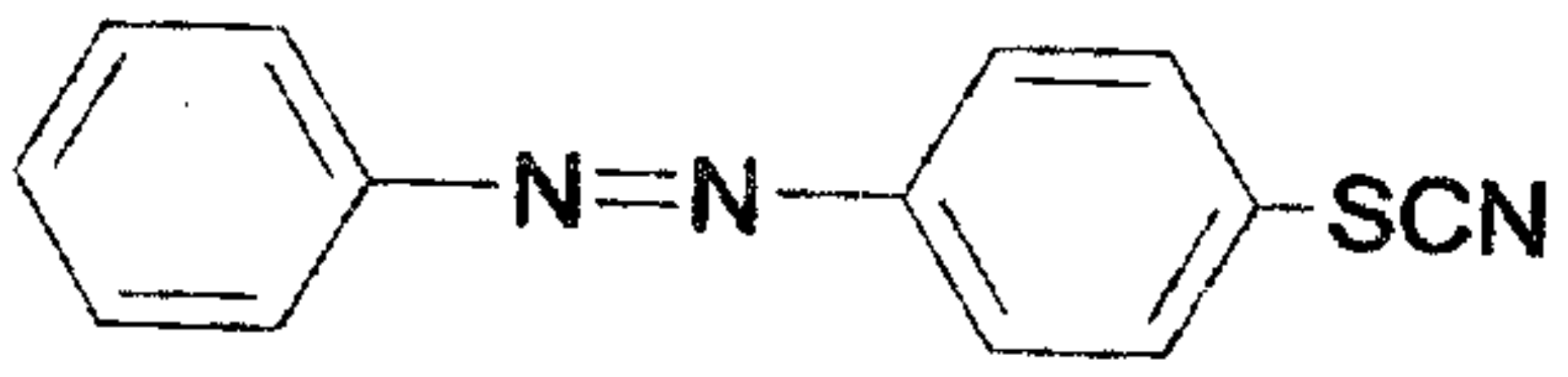
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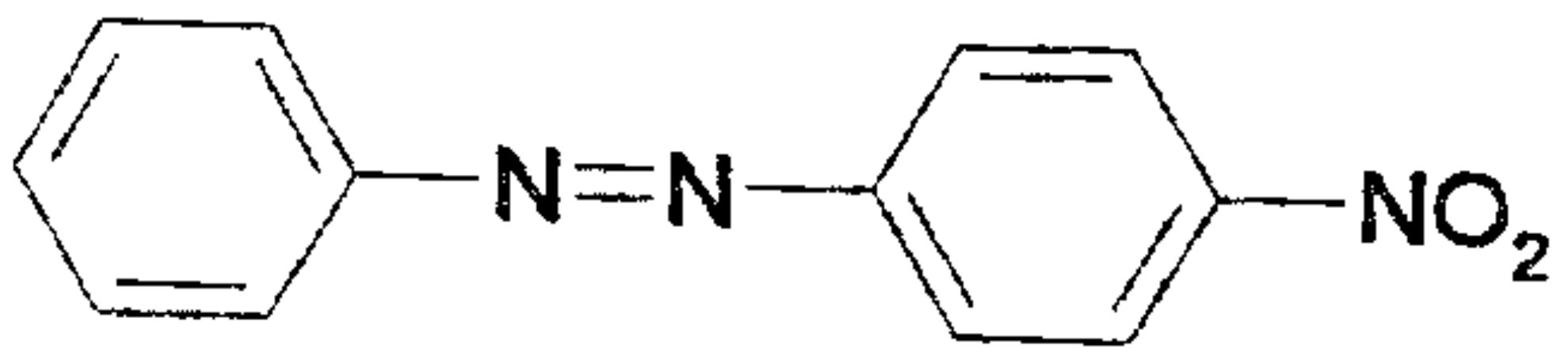
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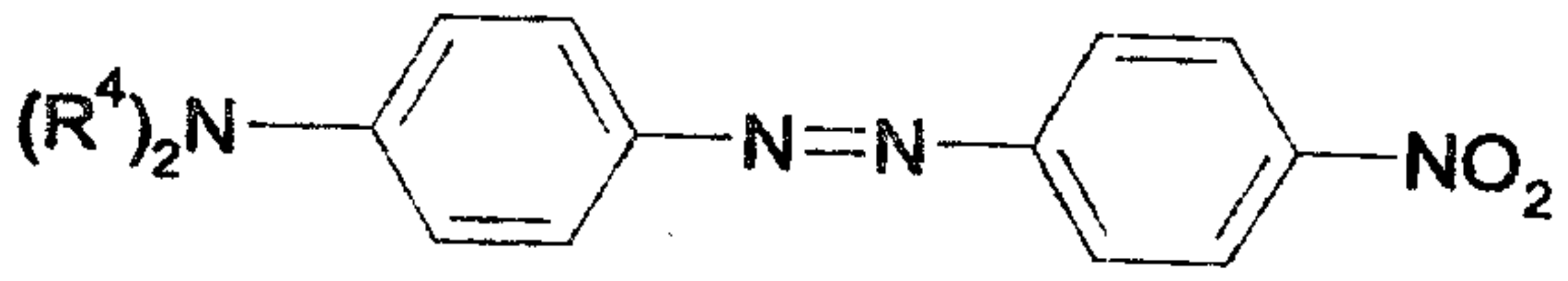
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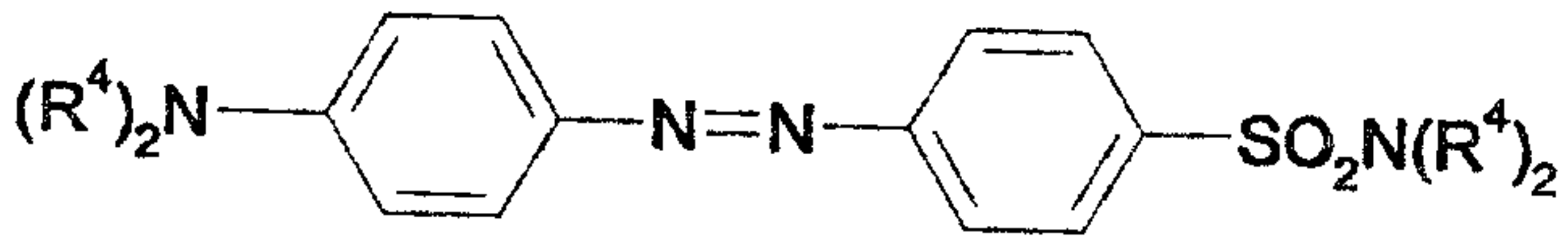
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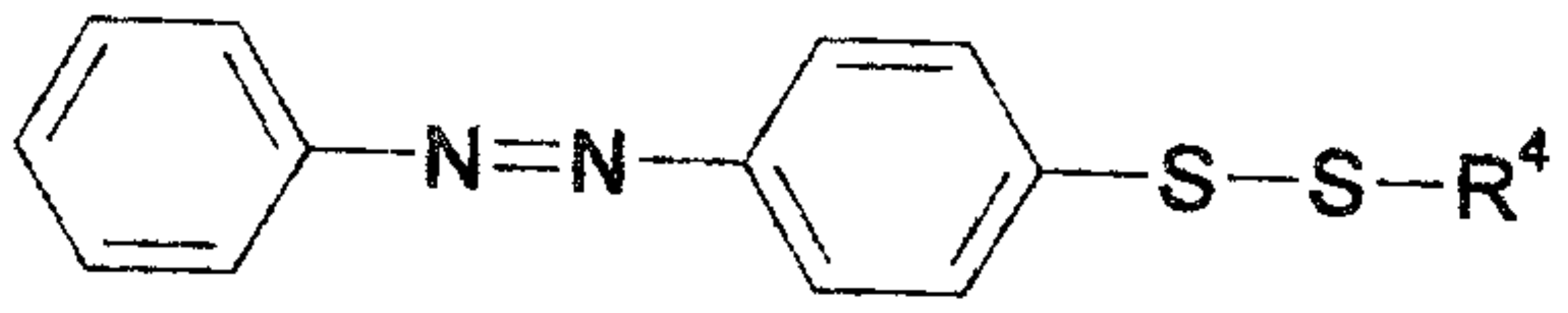
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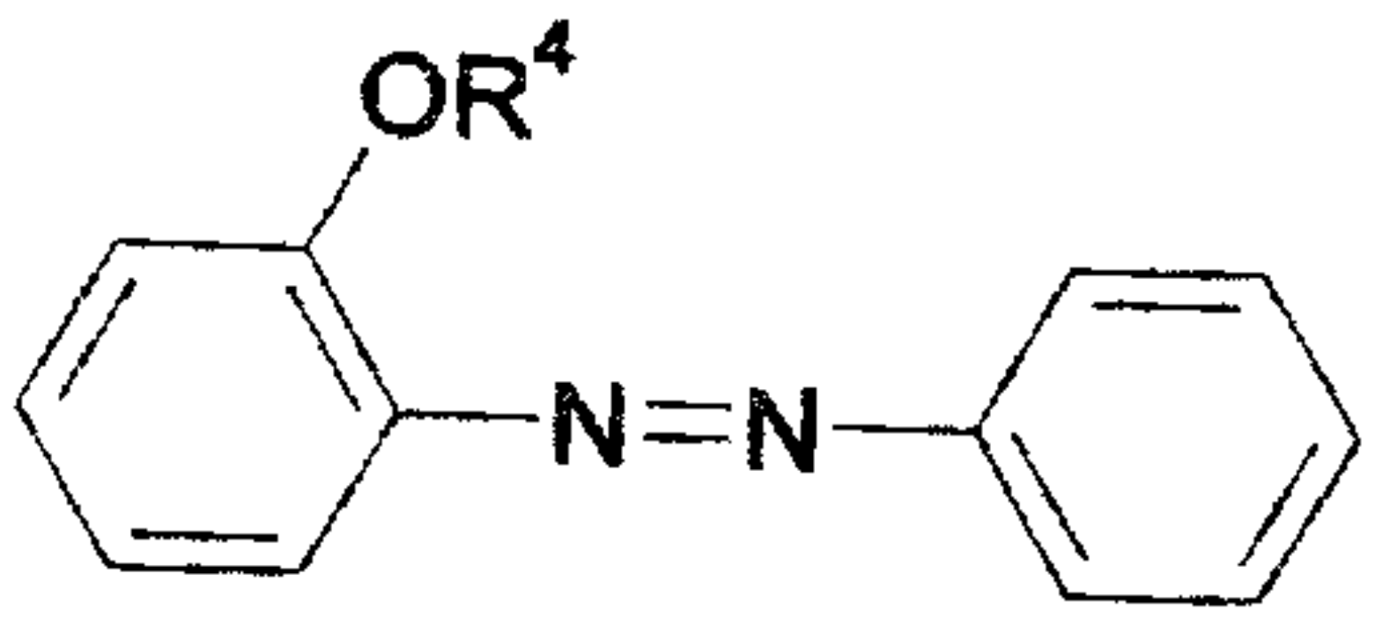
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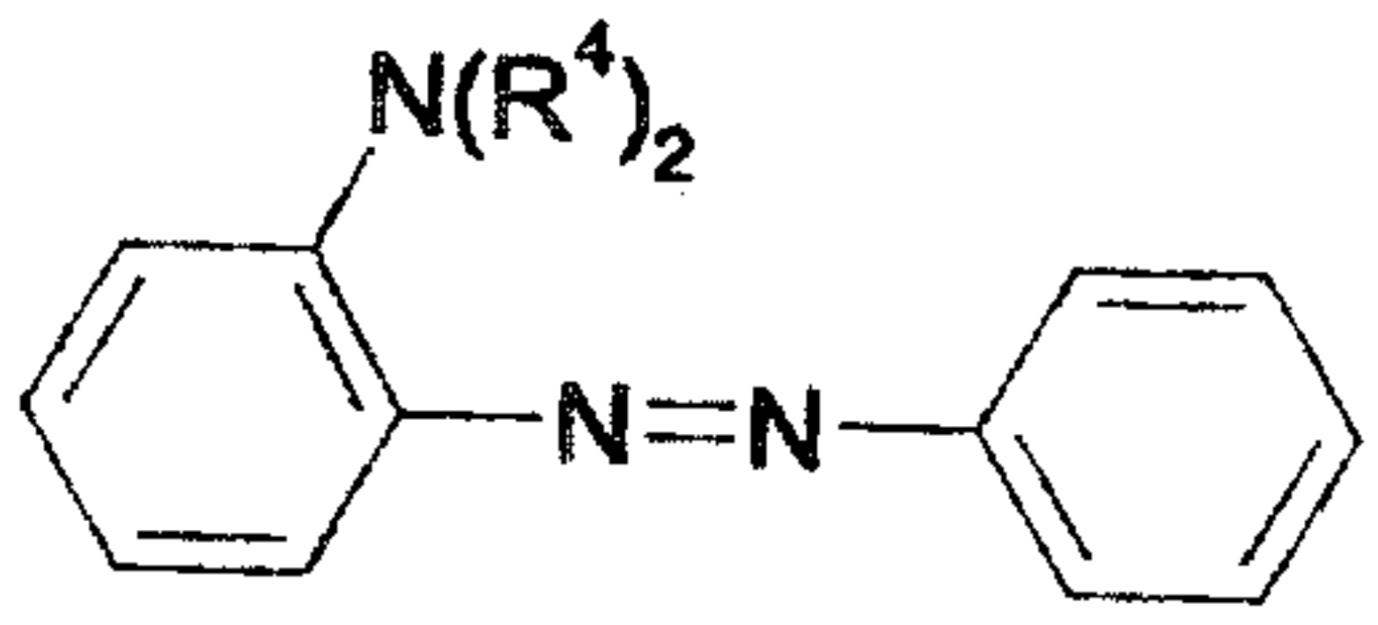
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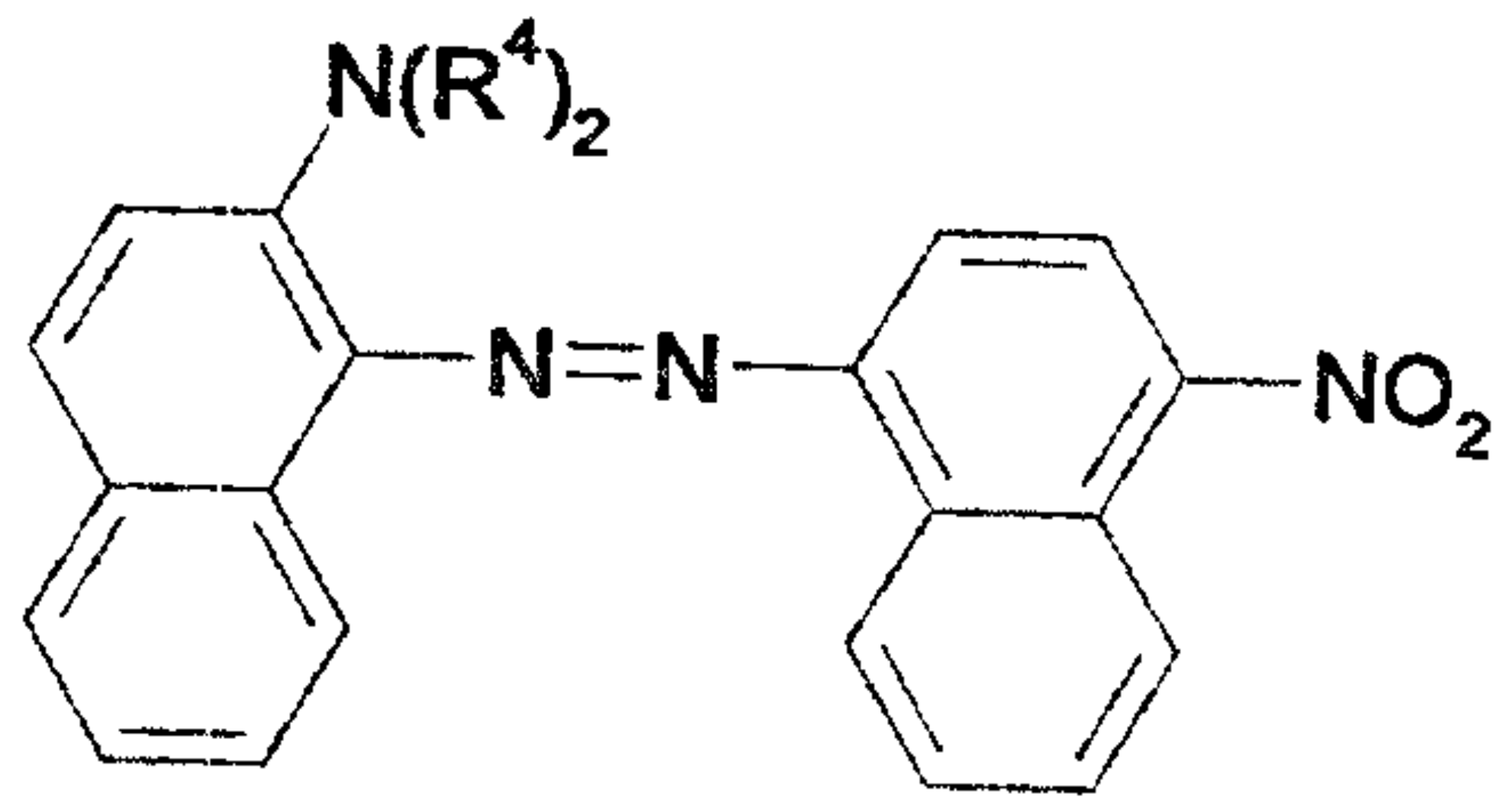
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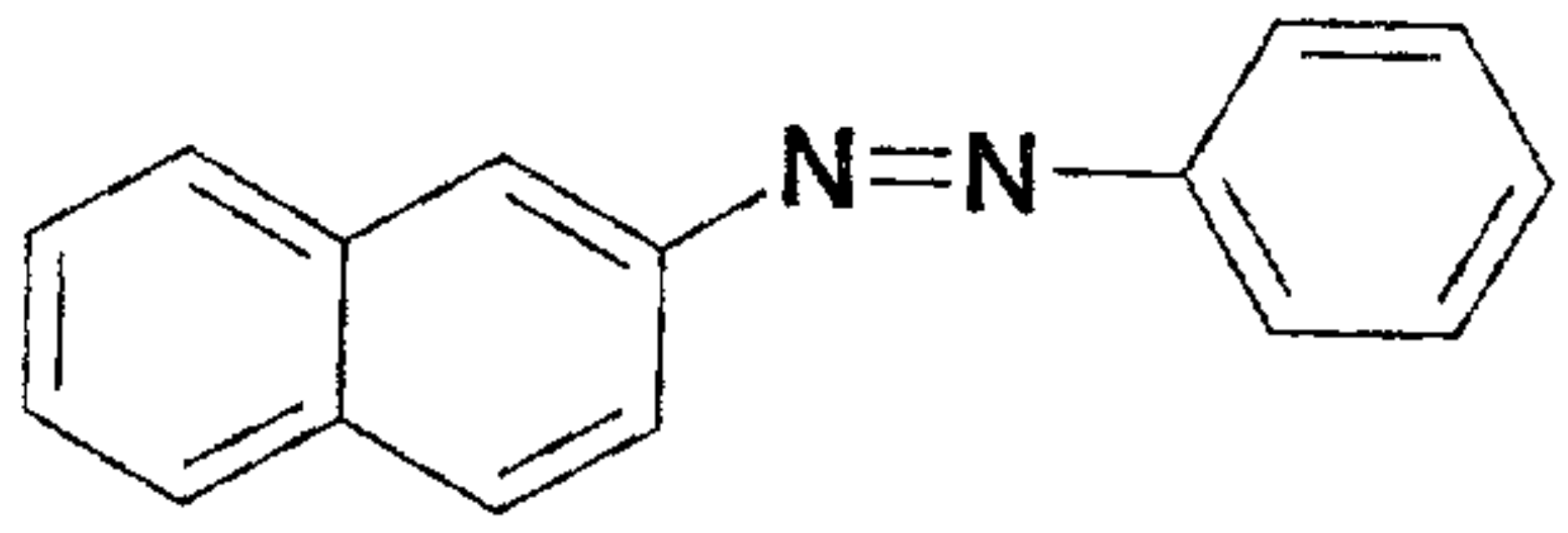
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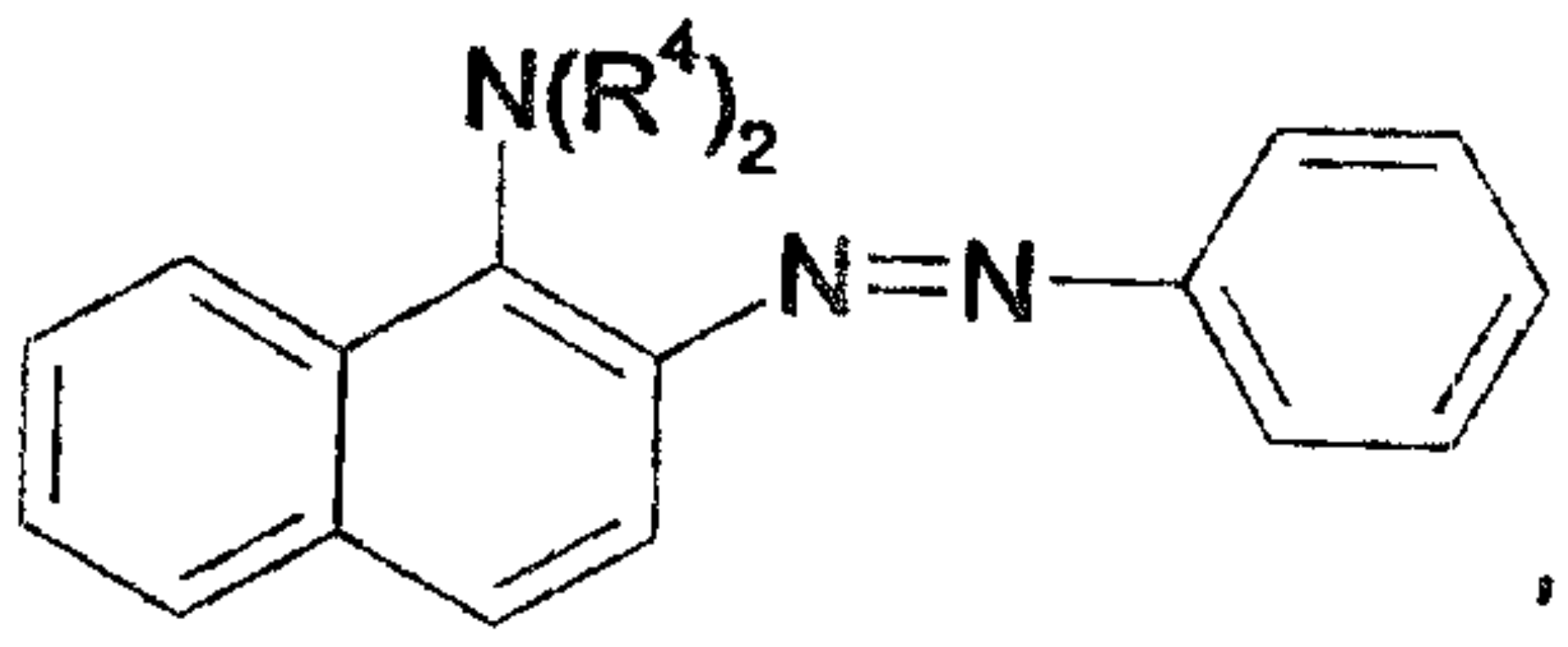
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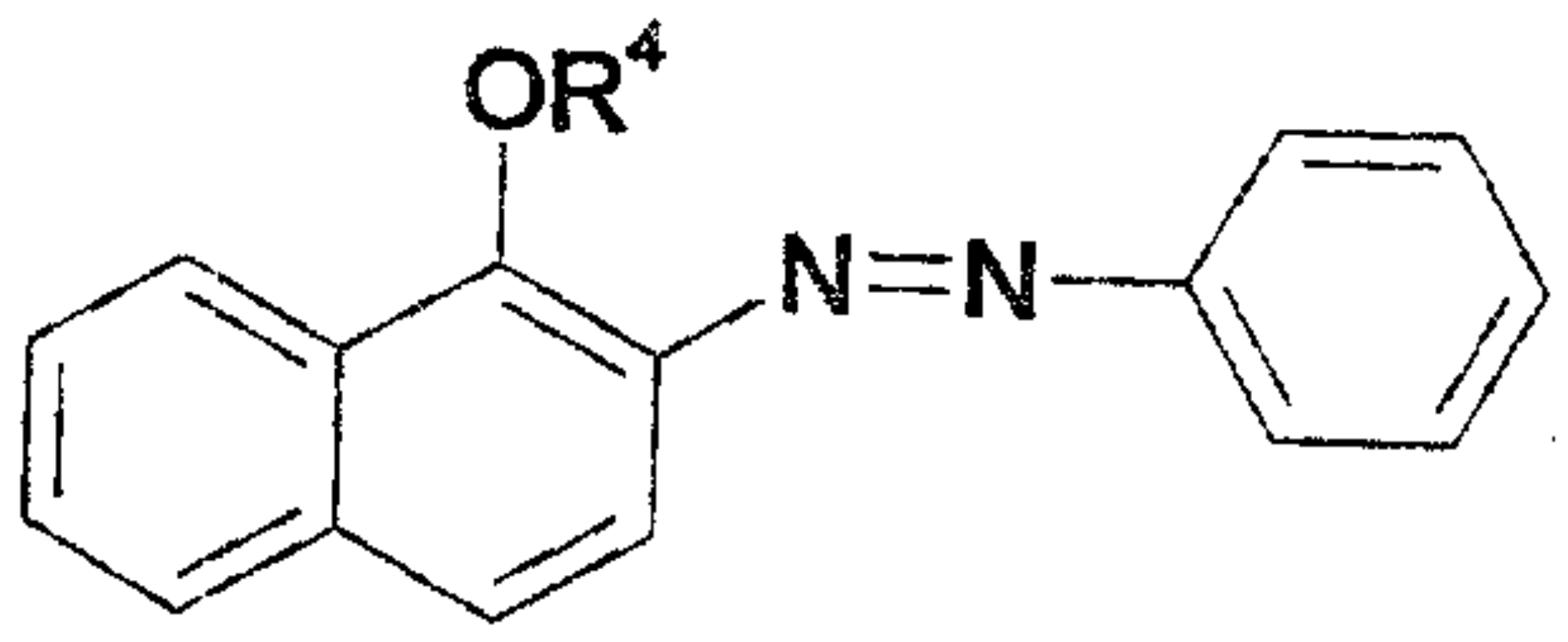
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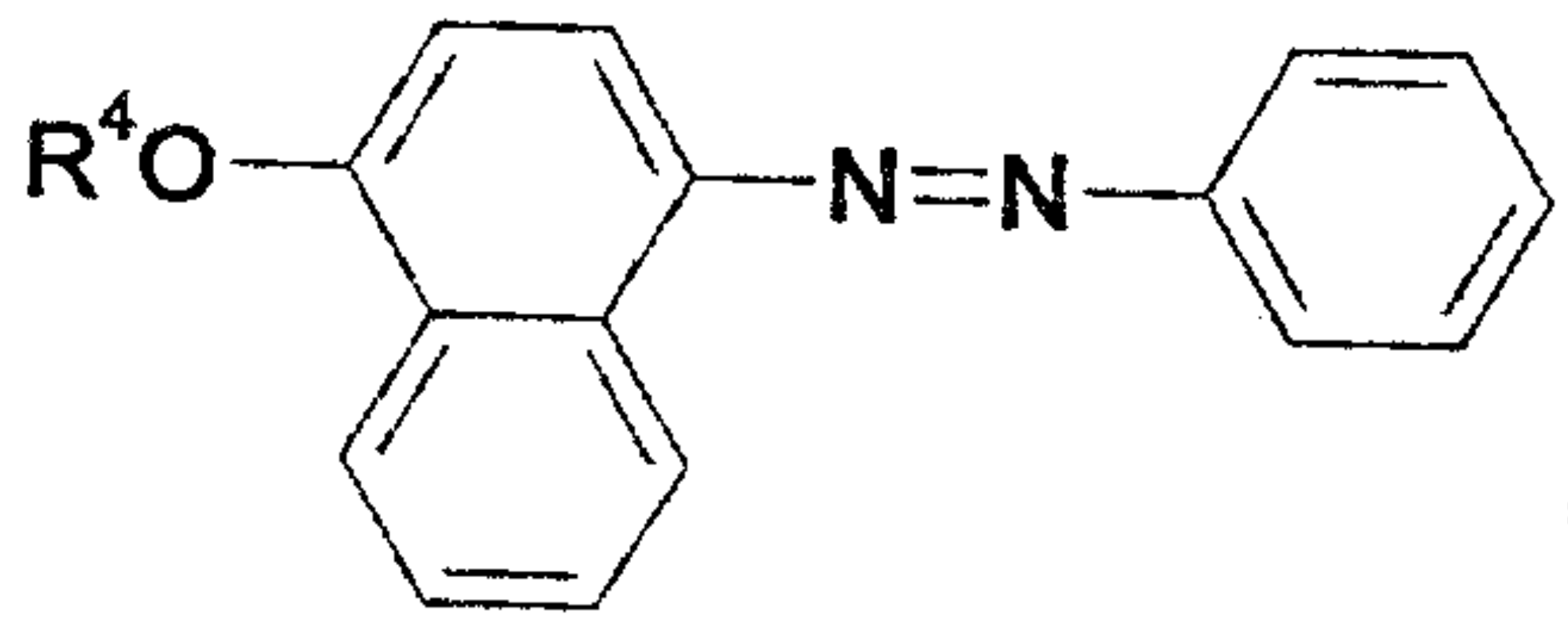
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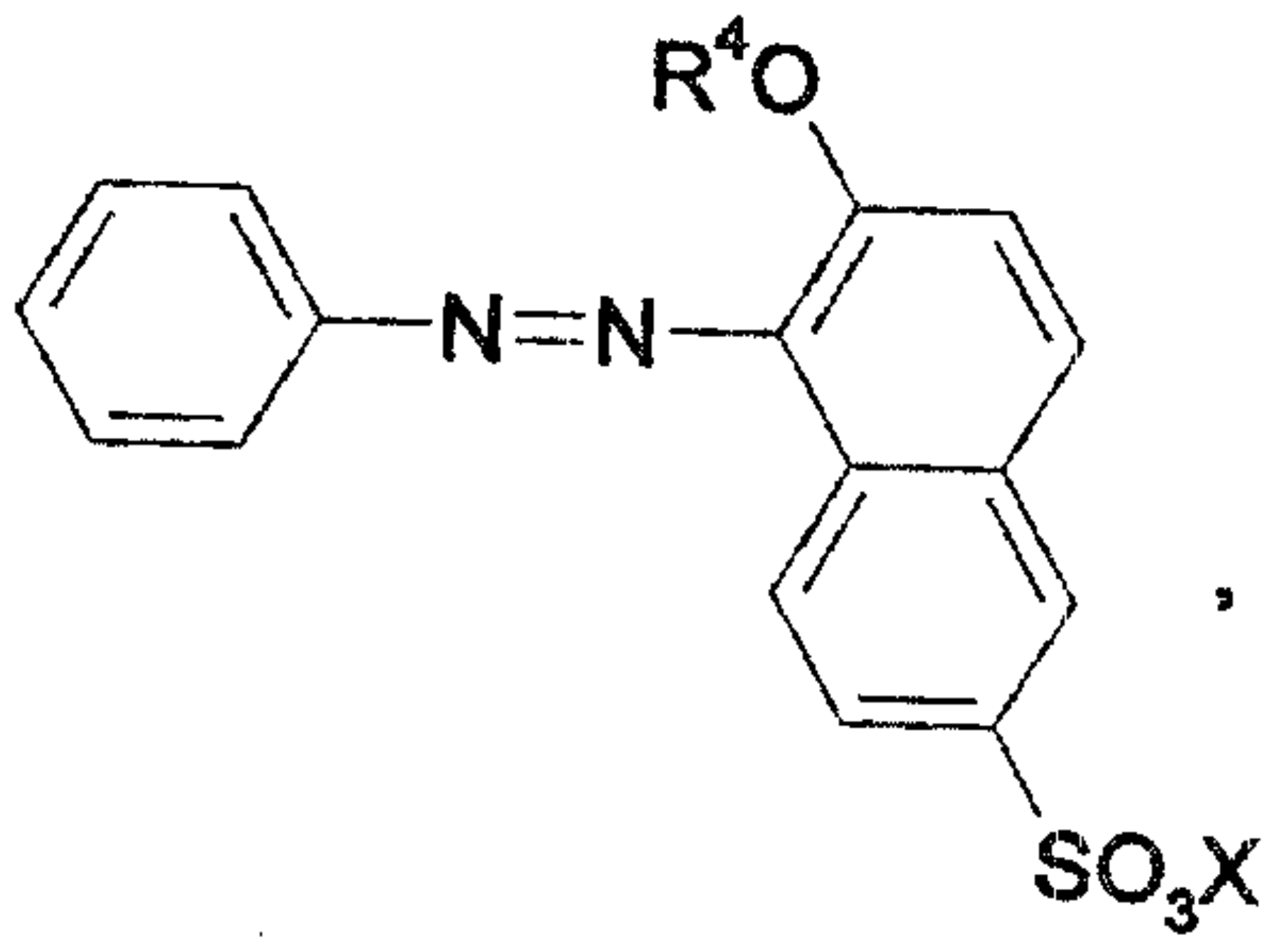
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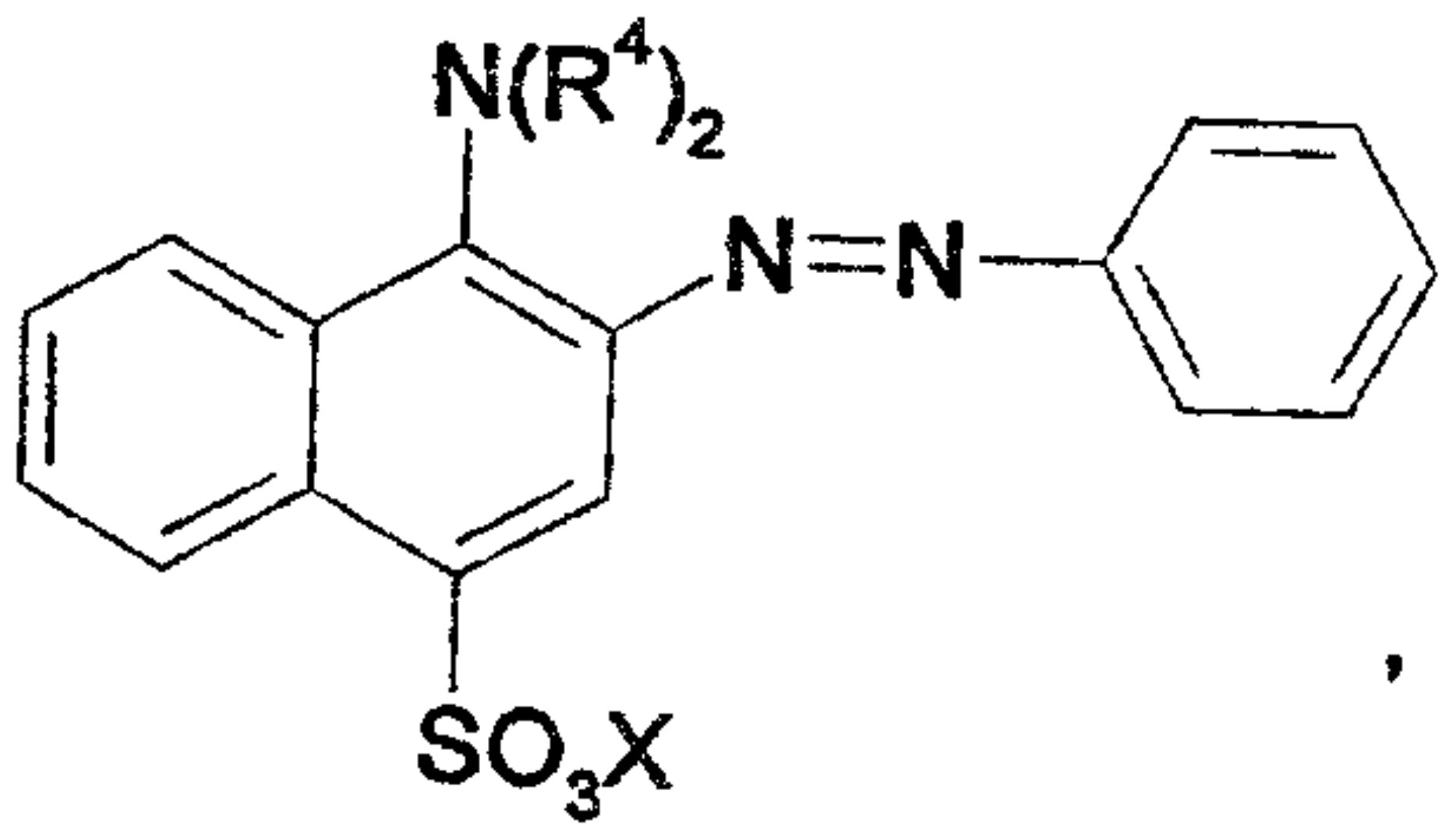
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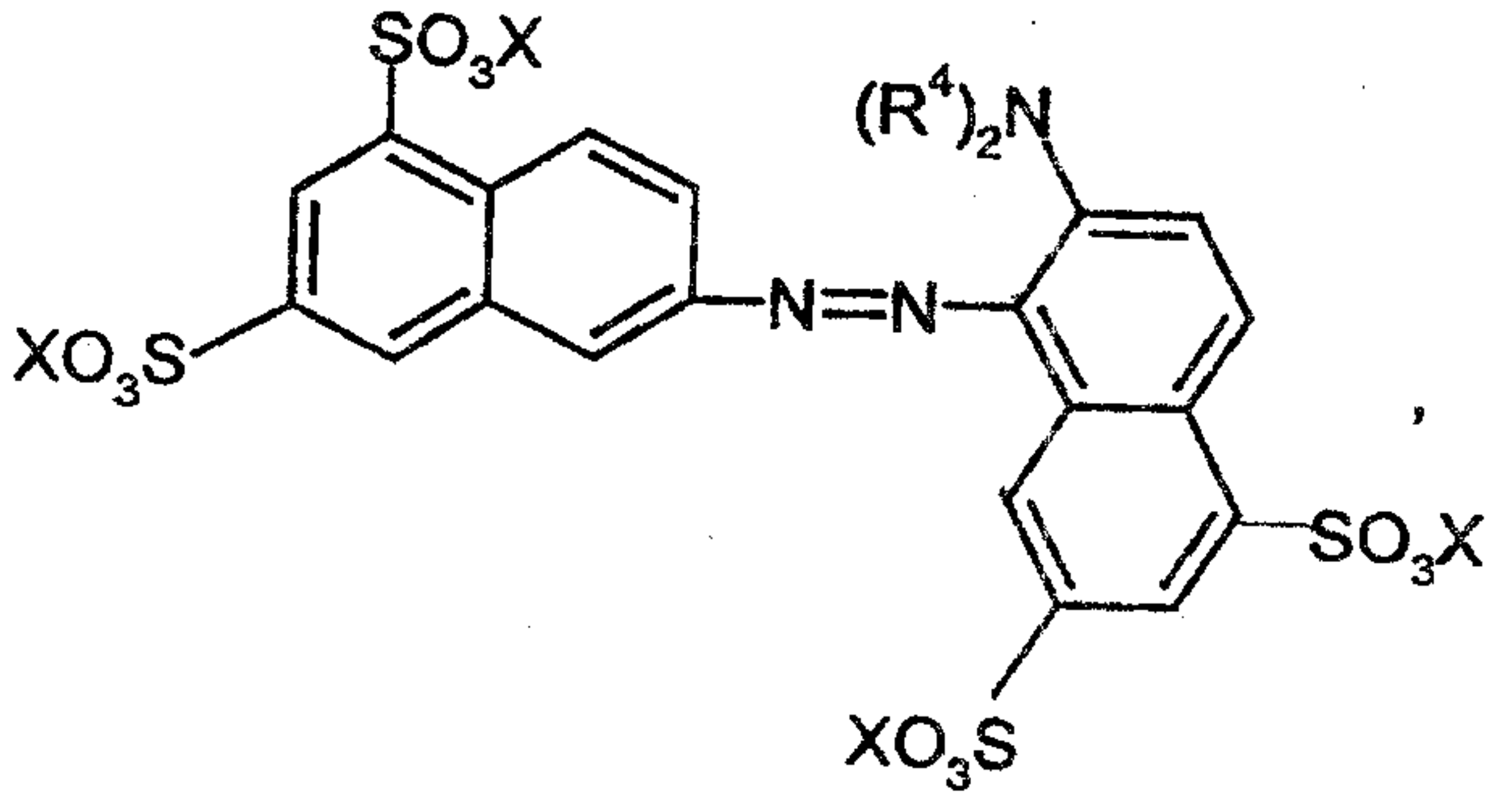
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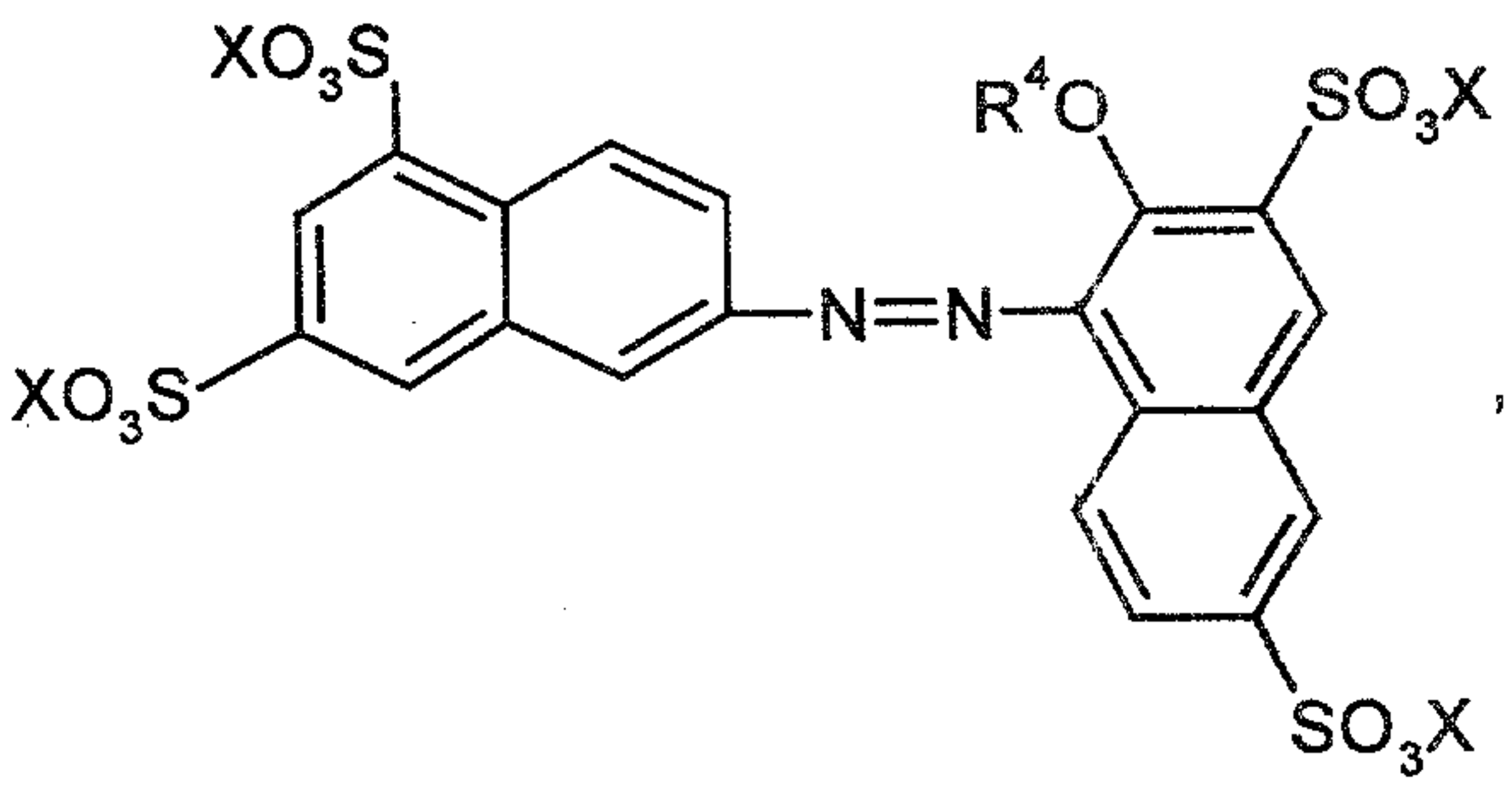

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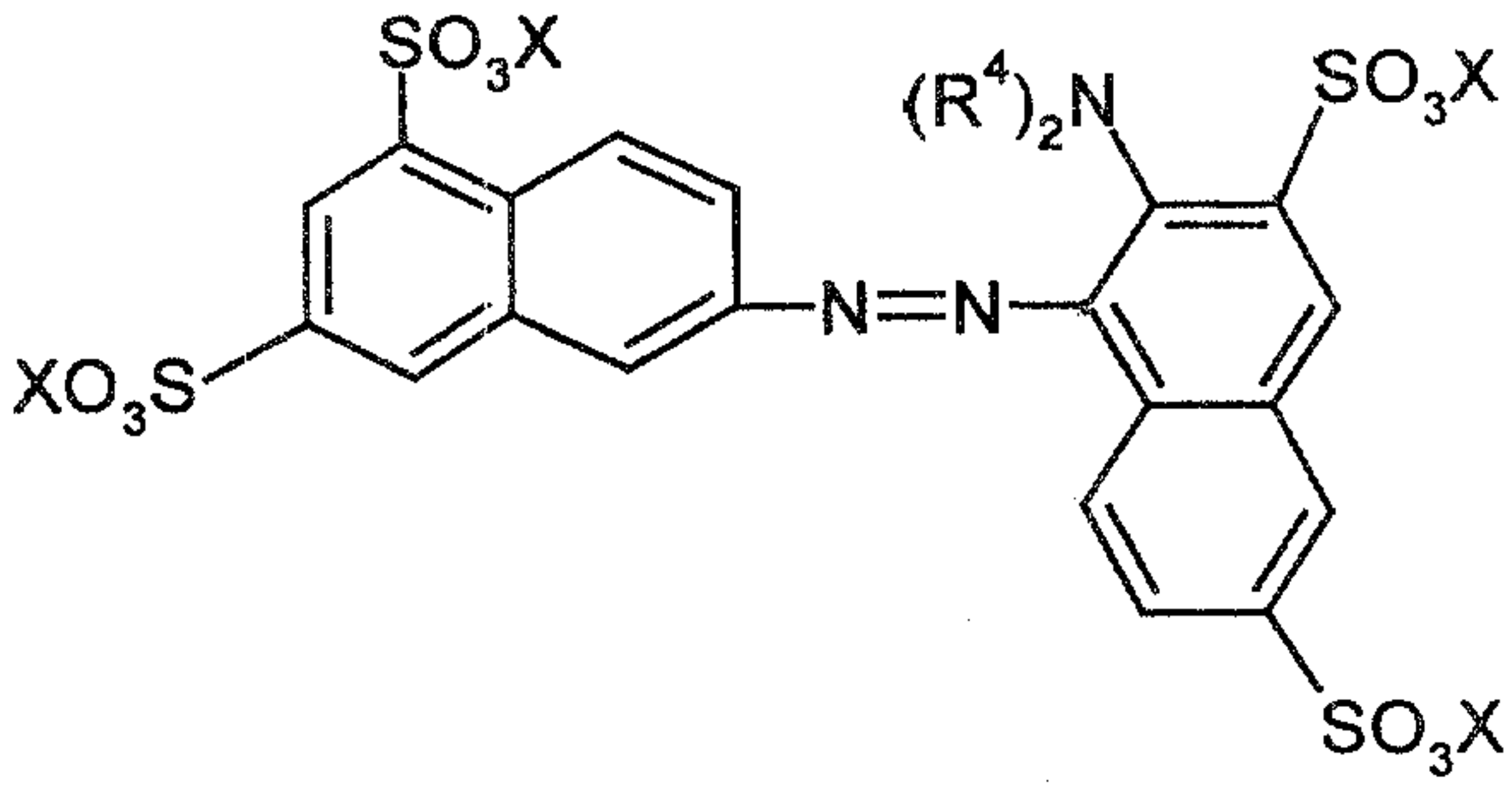

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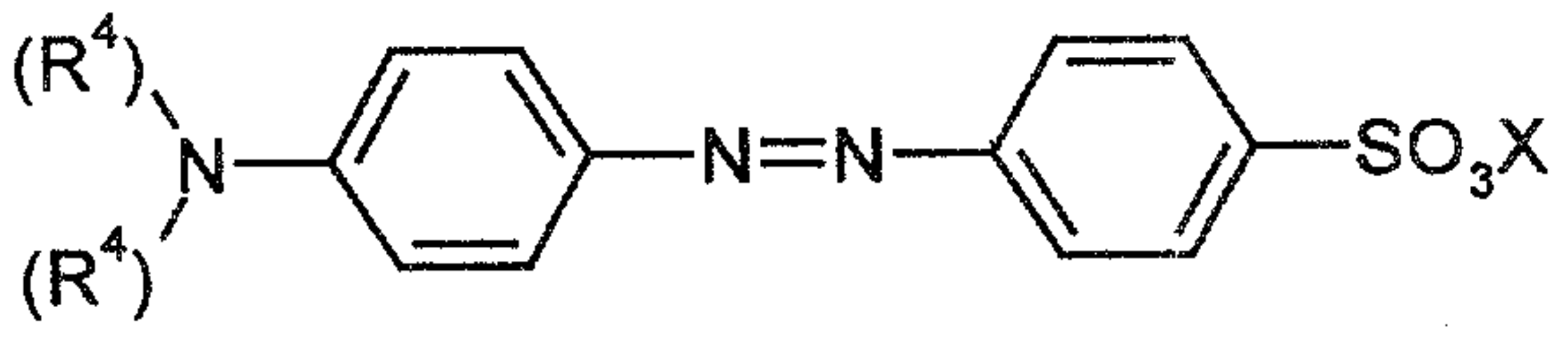

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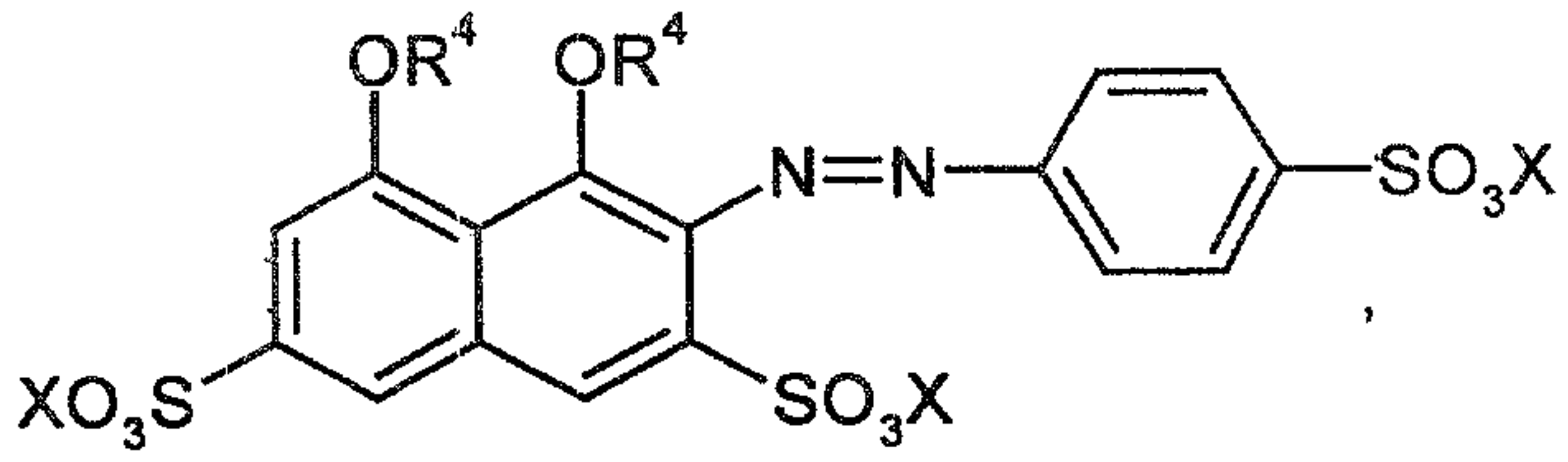

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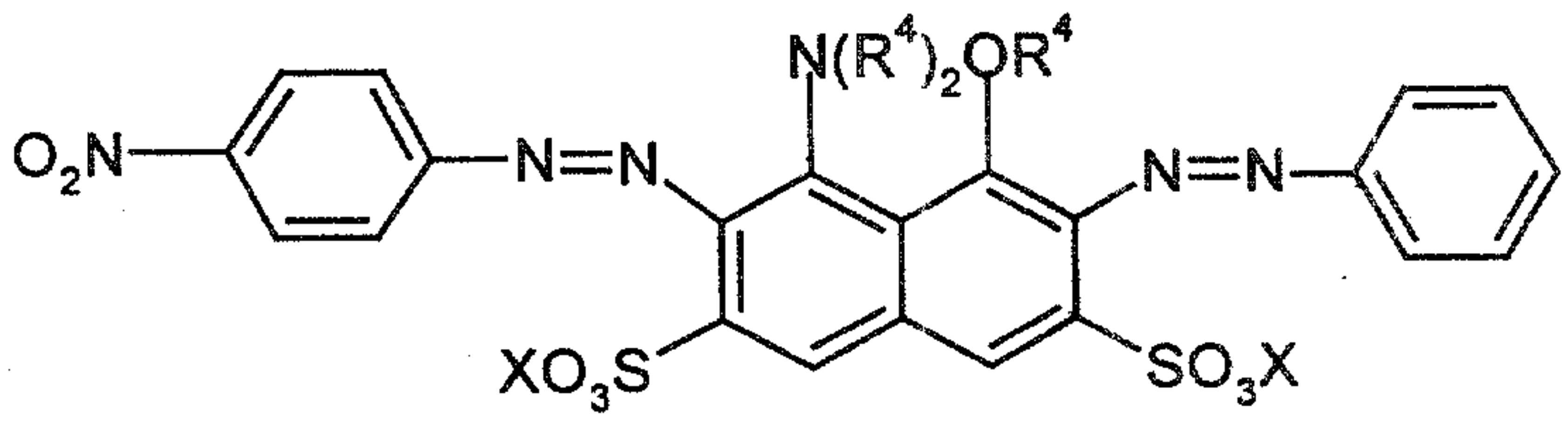

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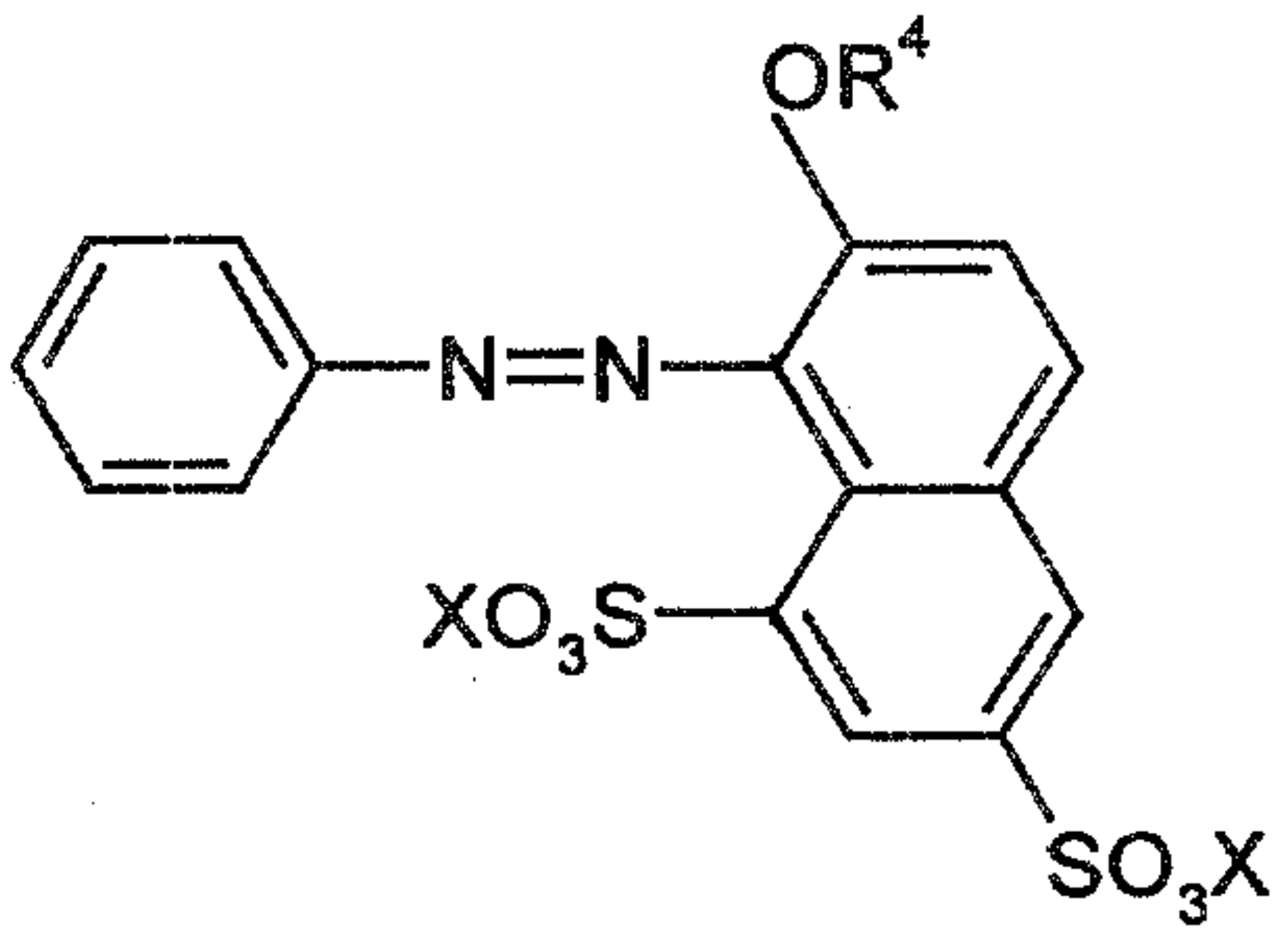

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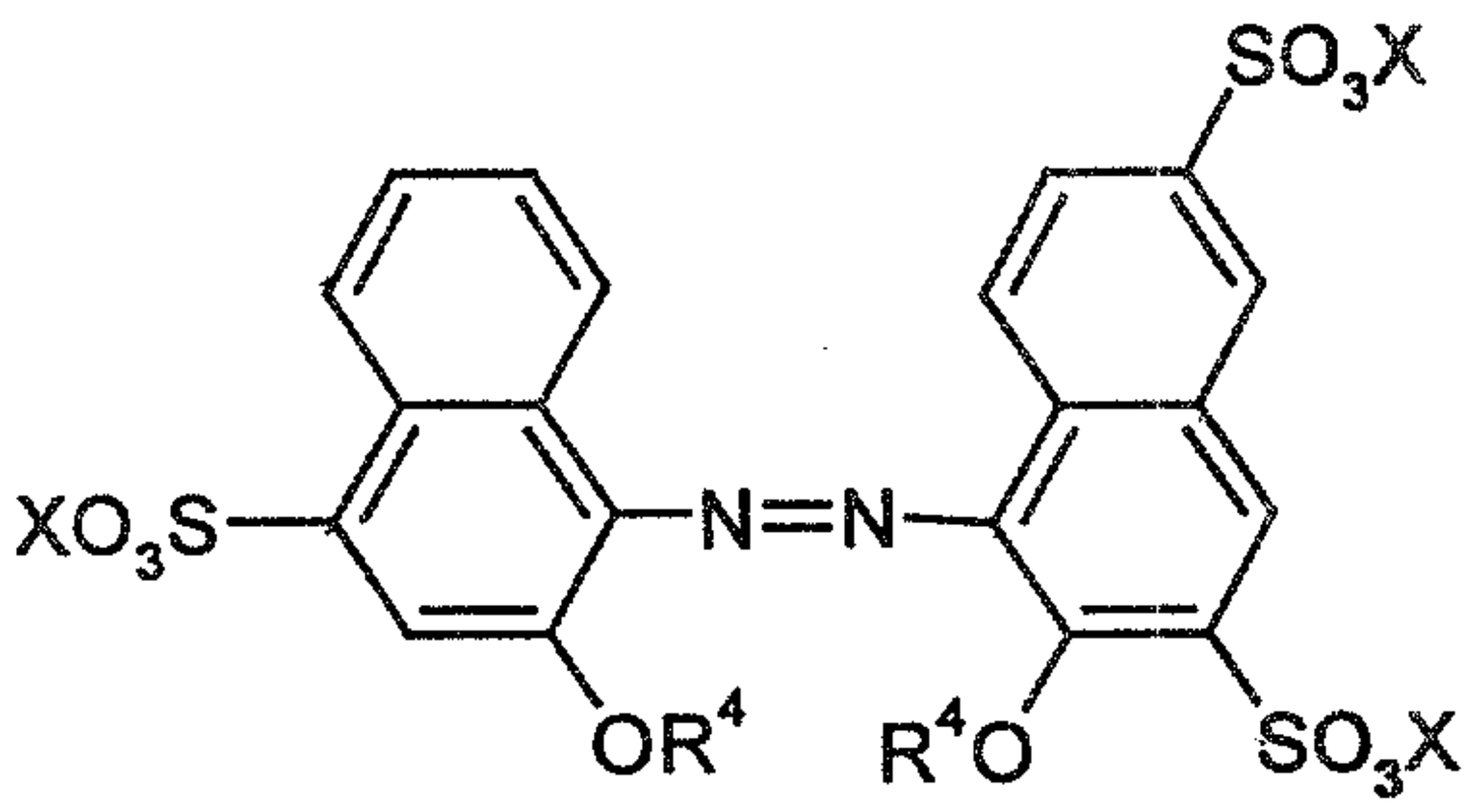

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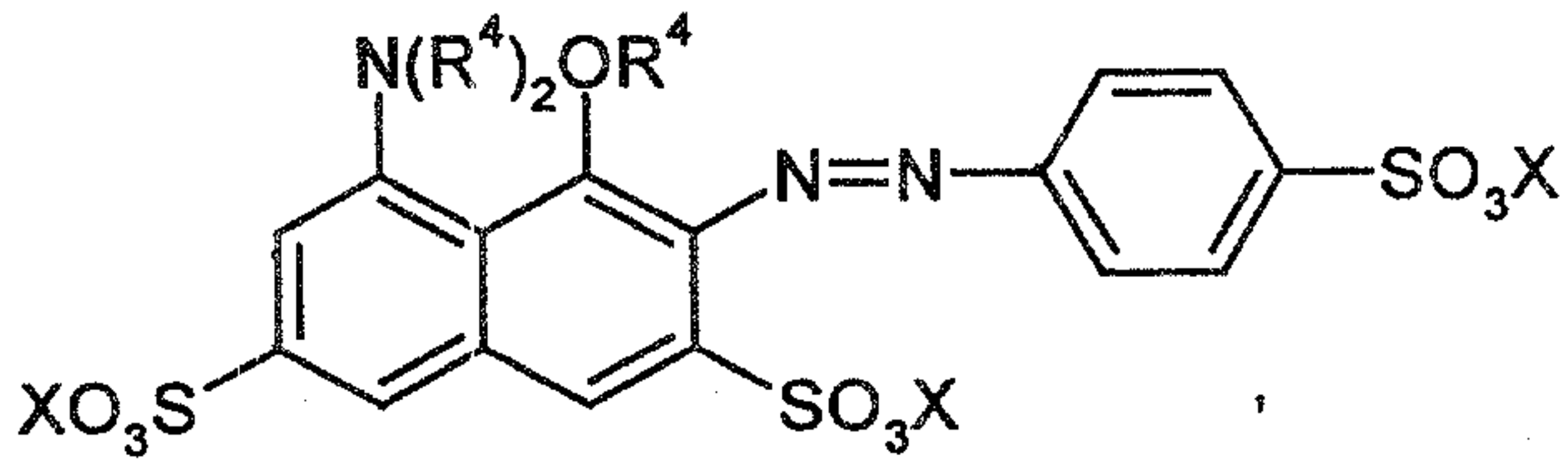

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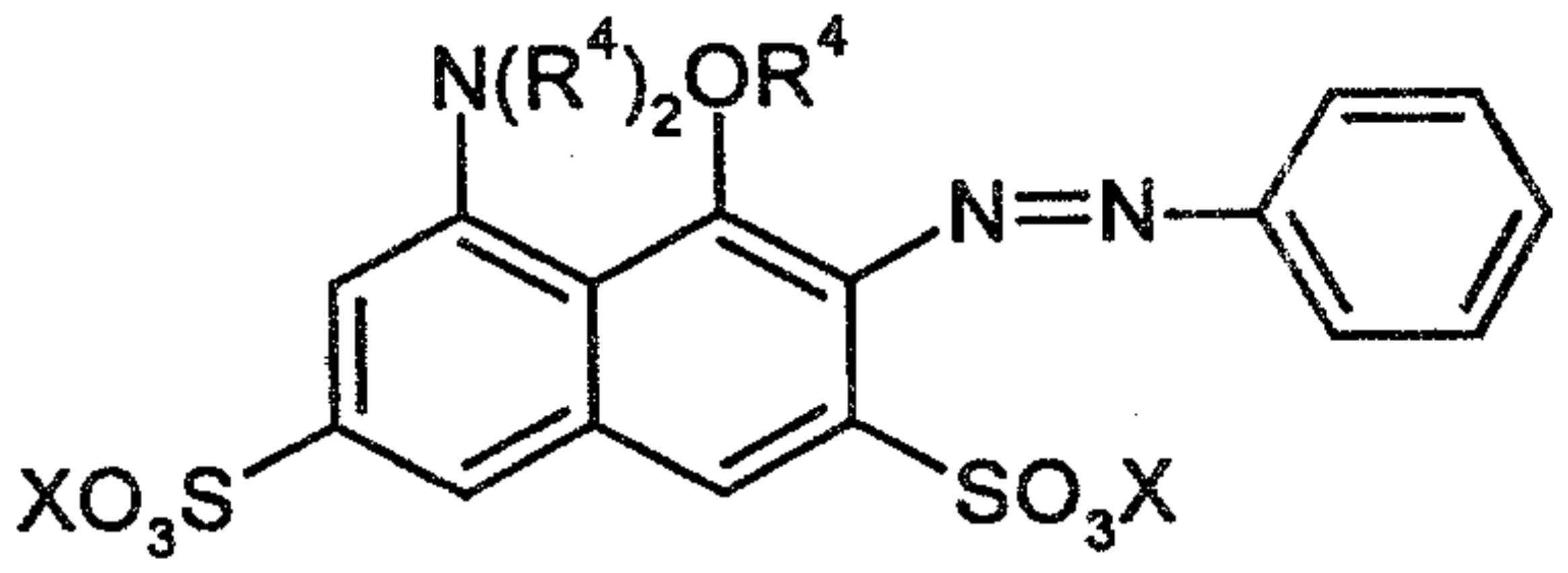

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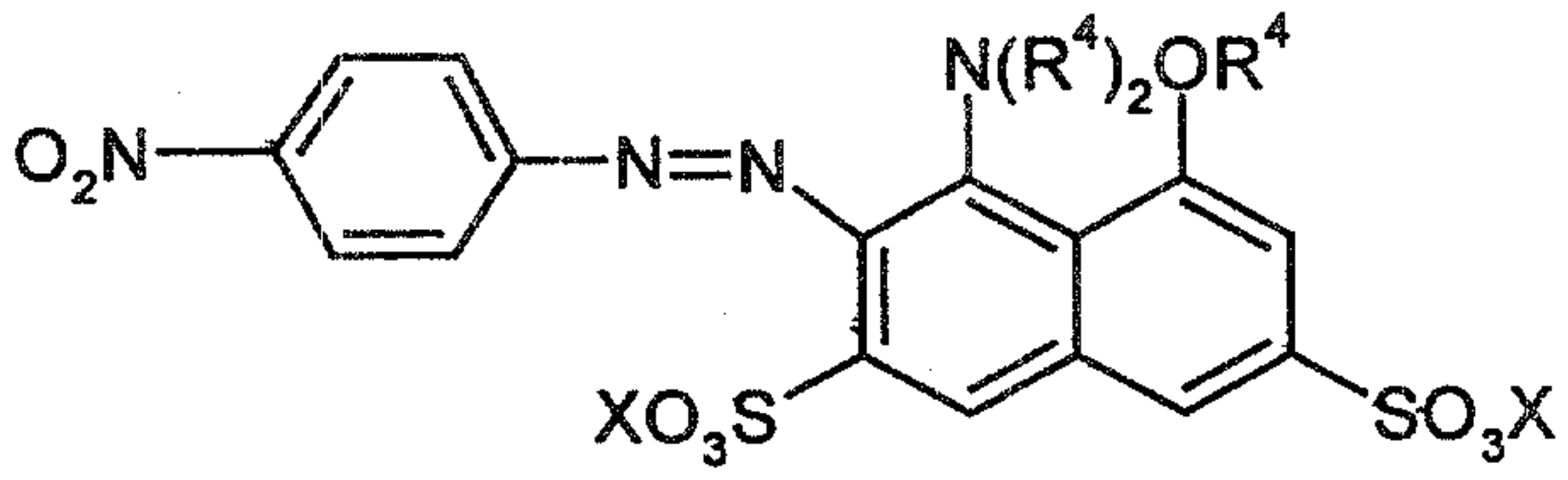

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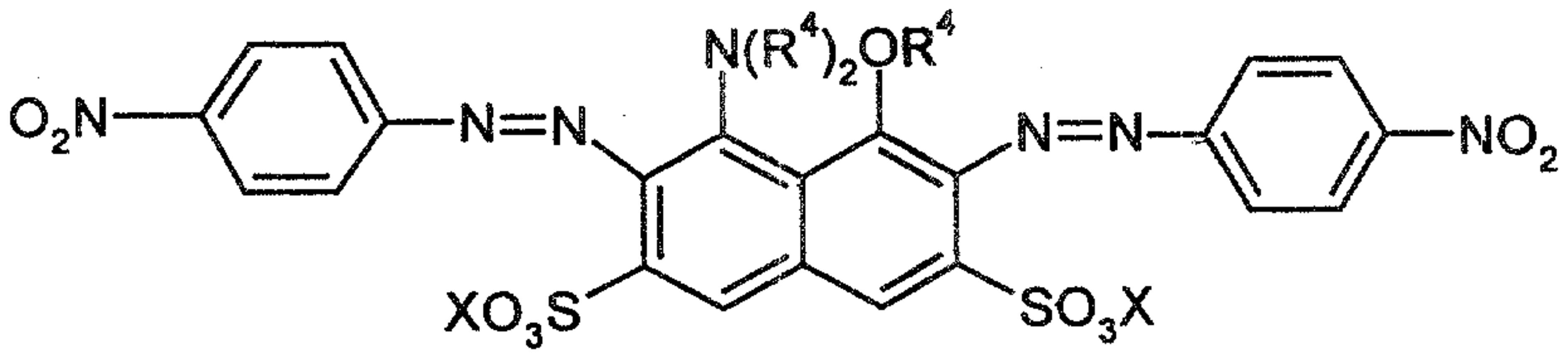

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where X = H, alkali metal ions or ammonium ions

Carbon-containing materials which may be used are carbon black, graphite powder, graphite fibres, carbon fibres, carbon fibrils, carbon nanotubes, woven carbon fabric, vitreous carbon products, activated carbon, coal, coke or diamond.

Any known kind of carbon black may be used as the carbon-containing material, such as for example furnace black, gas black, channel black, lamp black, thermal black, acetylene black, plasma black, inversion black, known from DE 195 21 565, carbon blacks containing Si, known from WO 98/45361 or DE 19613796, or carbon blacks containing metal, known from WO 98/42778, arc blacks and carbon-containing materials which are secondary products of chemical production processes.

Carbon-containing materials which are used as a reinforcing filler in rubber compounds may be used. Pigment blacks may be used. Further carbon-containing materials may be: conductive carbon-containing material, carbon-containing material for UV stabilisation, carbon-containing material as a filler in systems other than rubber, such as for example in bitumen, plastics, carbon-containing material as a reducing agent in metallurgy.

The carbon-containing material may be activated by upstream reactions.

The present invention also provides a process for the production of the carbon-containing material with organic groups according to the invention, which process is characterised in that carbon-containing material is reacted with organic compounds of the general formula I.

The organic compound of the general formula I may be applied onto the carbon-containing material by being incorporated therein or sprayed thereon. The organic compound of the general formula I may be applied as a powder, melt or solution. It may be particularly advantageous to apply the organic compound during the production of the carbon-containing material, wherein addition of the organic compound of the general formula I preferably proceeds at a point which is at the necessary temperature. The reaction of the carbon-containing material may preferably be carried out without solvents, but may also be carried out in a solvent, preferably highly volatile organic solvents. The reaction for modifying the carbon-containing material may be carried out at temperatures of -80° to 250°C, preferably of 80° to 250°C. If the reaction proceeds during the production of the carbon-containing material, the temperatures may be between 250° and 1500°C.

The reaction of the carbon-containing material with the organic compound of the general formula I may proceed in a quantity ratio of 99.99:0.01-0.01:99.99, preferably of 50:1-1:50.

The reaction of the carbon-containing material with the organic compound of the general formula I may be performed in a pressure range from 1 mbar to 250 bar, preferably from 100 mbar to 50 bar.

According to one aspect of the invention there is provided a carbonaceous material with organic groups, obtained by a process comprising:

contacting an organic compound of formula I with a carbonaceous material during the production of said carbonaceous material, wherein said contacting is under conditions that are sufficient to cause a reaction;

$$R^1{-}N{=}N{-}R^2 \qquad (I)$$

wherein R^1 and R^2 are identical or different, and are aryl groups which are unsubstituted or substituted with one or more acceptor substituents or one or more donor substituents; and

wherein the conditions that are sufficient to cause reaction occur within a temperature range of from 250° to 1500°C.

According to a further aspect of the invention there is provided a process for the production of a carbonaceous material with organic groups comprising:

contacting an organic compound of formula I with a carbanaceous material during the production of said carbonaceous material, wherein said contacting is under conditions that are sufficient to cause a reaction;

$$R^1{-}N{=}N{-}R^2 \qquad (I)$$

wherein R^1 and R^2 are identical or different, and are aryl groups which are unsubstituted or substituted with one or more acceptor substituents or one or more donor substituents; and

wherein the conditions that are sufficient to cause reaction occur within a temperature range of from 250° to 1500°C.

According to another aspect of the invention there is provided a carbonaceous material with organic groups, obtained by a process comprising:

contacting an organic compound of formula I with a carbonaceous material under conditions that are sufficient to cause a reaction;

$$R^1{-}N{=}N{-}R^2 \qquad (I)$$

wherein R^1 and R^2 are identical or different, and are aryl groups which are unsubstituted or substituted with one or more acceptor substituents or one or more donor substituents;

wherein the ratio of the carbonaceous material to the organic compound of formula I ranges from 99.99:0.01 to 0.01:99.99; and

wherein the conditions that are sufficient to cause a reaction occur within a temperature range of from -80° to 300°C.

According to yet another aspect of the invention there is provided a process for the production of the carbonaceous material with organic groups comprising:

contacting an organic compound of formula I with a carbonaceous material under conditions that are sufficient to pause a reaction;

$$R^1{-}N{=}N{-}R^2 \qquad (I)$$

wherein R^1 and R^2 are identical or different, and are aryl groups which are unsubstituted or substituted with one or more acceptor substituents or one or more donor substituents;

wherein the ratio of the carbonaceous material to the organic compound of formula I ranges from 99.99:0.01 to 0.01:99.99; and

wherein the conditions that are sufficient to cause a reaction occur within a temperature range of from -80° to 300°C.

The present invention also provides a dispersion which is characterised in that it contains the carbon-containing material with organic groups according to the invention.

The organic groups may here be tailored to the particular medium.

Accordingly, carbon-containing materials with polar organic groups may be particularly suitable for polar media. Polar media may be solvents, such as for example alcohols, ketones, esters, acids, amines, halogenated solvents or oligomers or polymers with polar groups, such as for example carbonyl, ester, amino, carboxyl and/or hydroxyl groups. Carbon-containing materials with, for example, $-SO_3X$, COOX, OH (where X = H, alkali metal ions, ammonium ions), may be particularly suitable for aqueous media.

Carbon-containing materials with hydrophobic groups, such as for example alkyl, alkyloxy, aryl and/or hetaryl, may be used for hydrophobic media such as aliphatic, aromatic, heteroaliphatic and/or heteroaromatic hydrocarbons.

Organic groups, for example amino, carbonyl or halogen substituents, which are specifically matched to the media may be used for media which, with regard to their polarity, lie between relatively nonpolar, hydrophobic media and strongly polar media, for example ethers and/or mixtures of nonpolar and polar media.

The dispersions according to the invention may additionally contain one or more additives. These additives, for example monomeric, oligomeric or polymeric compounds, may be added for specific applications. These additives may enhance properties such as degree of dispersion, storage stability, frost stability, drying behaviour, film-forming ability, crosslinkability and/or adhesion to certain substrate materials, such as paper, metal, glass, polymers, fibres, leather, wood, concrete or rubber.

The carbon-containing materials with organic groups according to the invention may, for example, be used as a filler, reinforcing filler, UV stabiliser, conductive carbon black or pigment.

The carbon-containing materials with organic groups according to the invention may be used in rubber, plastics, printing inks, inks, inkjet inks, toners, lacquers, paints, paper, bitumen, concrete and other building materials. They may be used as reducing agents in metallurgy.

The carbon-containing materials according to the invention may be used to produce rubber compounds, in particular in tyre production.

The carbon-containing materials with organic groups according to the invention exhibit the advantage that

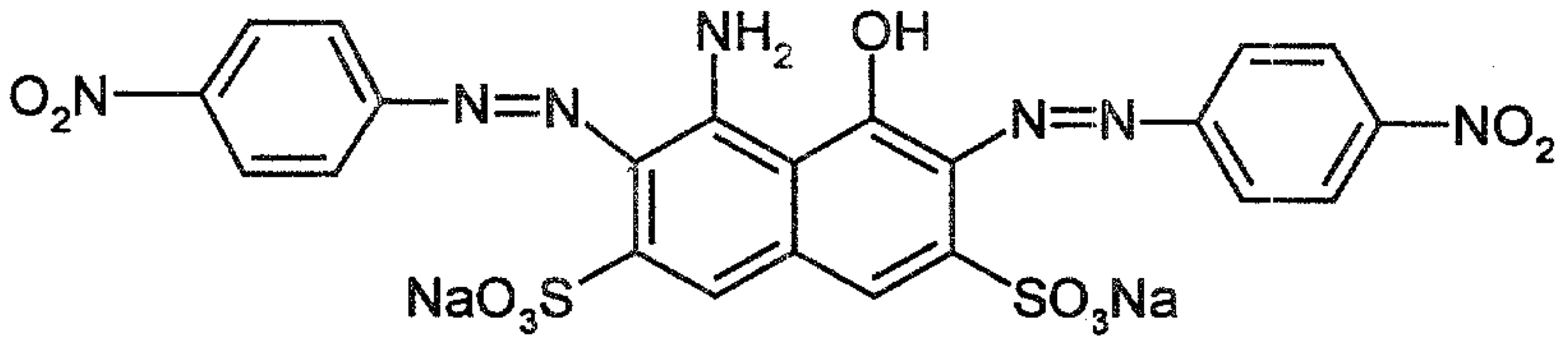
- polar-modified carbon-containing materials (for example modified with $-SO_3^-$ groups) are more readily dispersible in polar systems, primarily water,
- nonpolar-modified carbon-containing materials (for example modified with alkyl groups) are more readily dispersible in nonpolar systems, such as for example oils,
- suitably modified carbon-containing materials with polar or sterically bulky groups are electrostatically or sterically stabilised in the systems and no further auxiliary substances, such as for example wetting agents, are necessary for stabilisation,
- carbon-containing materials modified using the process according to the invention are better stabilised in dispersions and consequently result in lower viscosities

and exhibit better colouristic properties, such as colour depth and blue cast,

- carbon-containing material with bound dyes exhibits modified colour shades,
- carbon-containing material with substituents which are still reactive may be used for coupling and crosslinking in systems (for example rubber),
- reactive-modified carbon-containing materials permit binding of the carbon-containing material to the polymer,
- carbon-containing material may be produced with a low content of secondary products, salts, acids and moisture.

Examples:

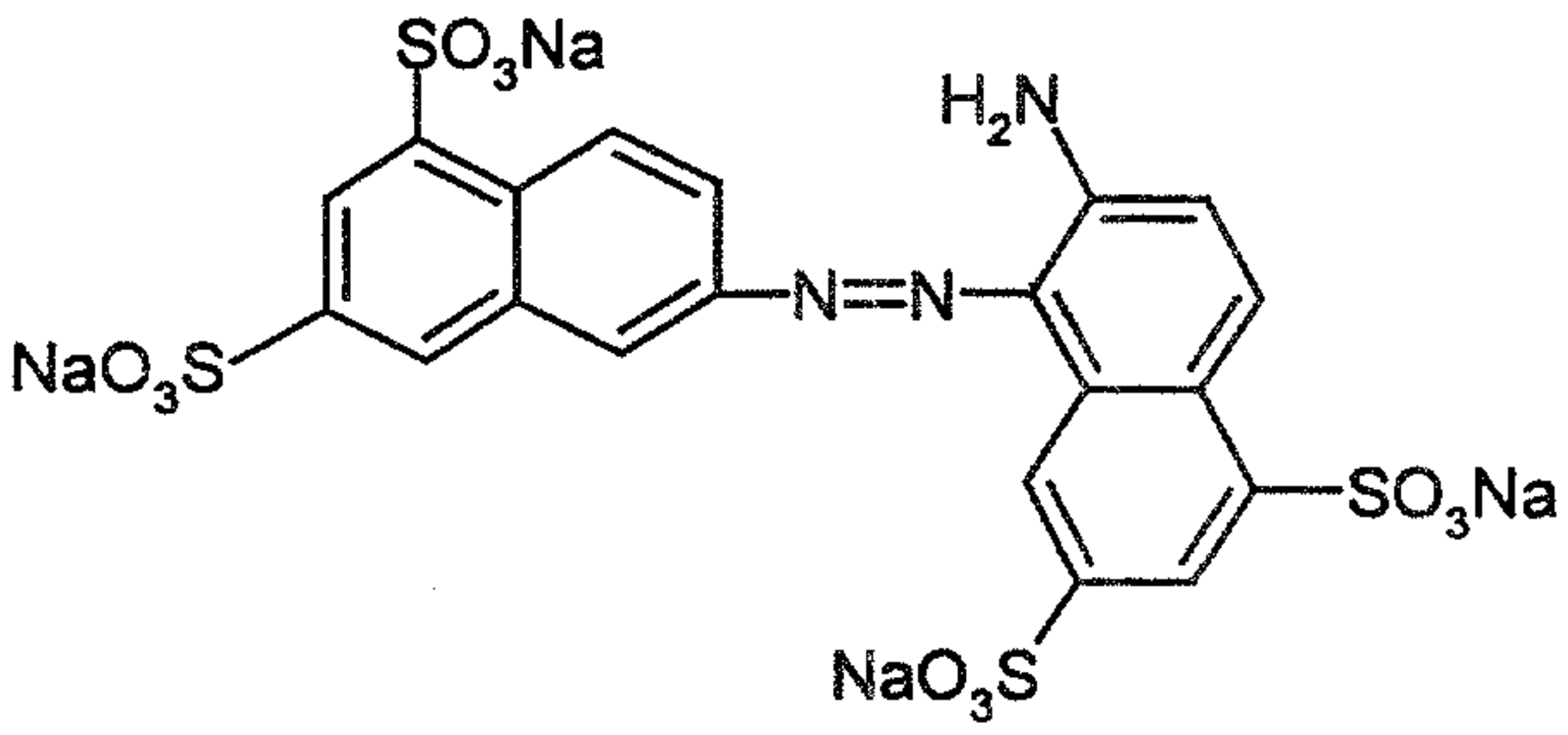
Example 1:
Synthesis of 8-amino-2,7-bis(4'-nitrobenzeneazo)-1-naphthol-3,6-disulfonic acid, disodium salt (1)



(1)

0.01 mol of 1-amino-8-naphthol-3,6-disulfonic acid are dissolved in 150 ml of water and then combined with 8 g of sodium acetate and 8 g of glacial acetic acid. The mixture is cooled to 10°C. 0.022 mol of the diazonium salt of 4-nitroaniline ("Organikum", 19th edition, p. 560, Verlag Johann Ambrosius Barth Leipzig) are slowly added at this temperature. The mixture is then stirred overnight, after which 200 ml of water are added and the mixture salted out with sodium chloride. The product is removed by suction filtration and dried in a desiccator.

Example 2
Synthesis of 2-amino-1-(naphthyl-2'-azo)-naphthyl-5,5',7,7'-tetrasulfonic acid, tetrasodium salt (2)

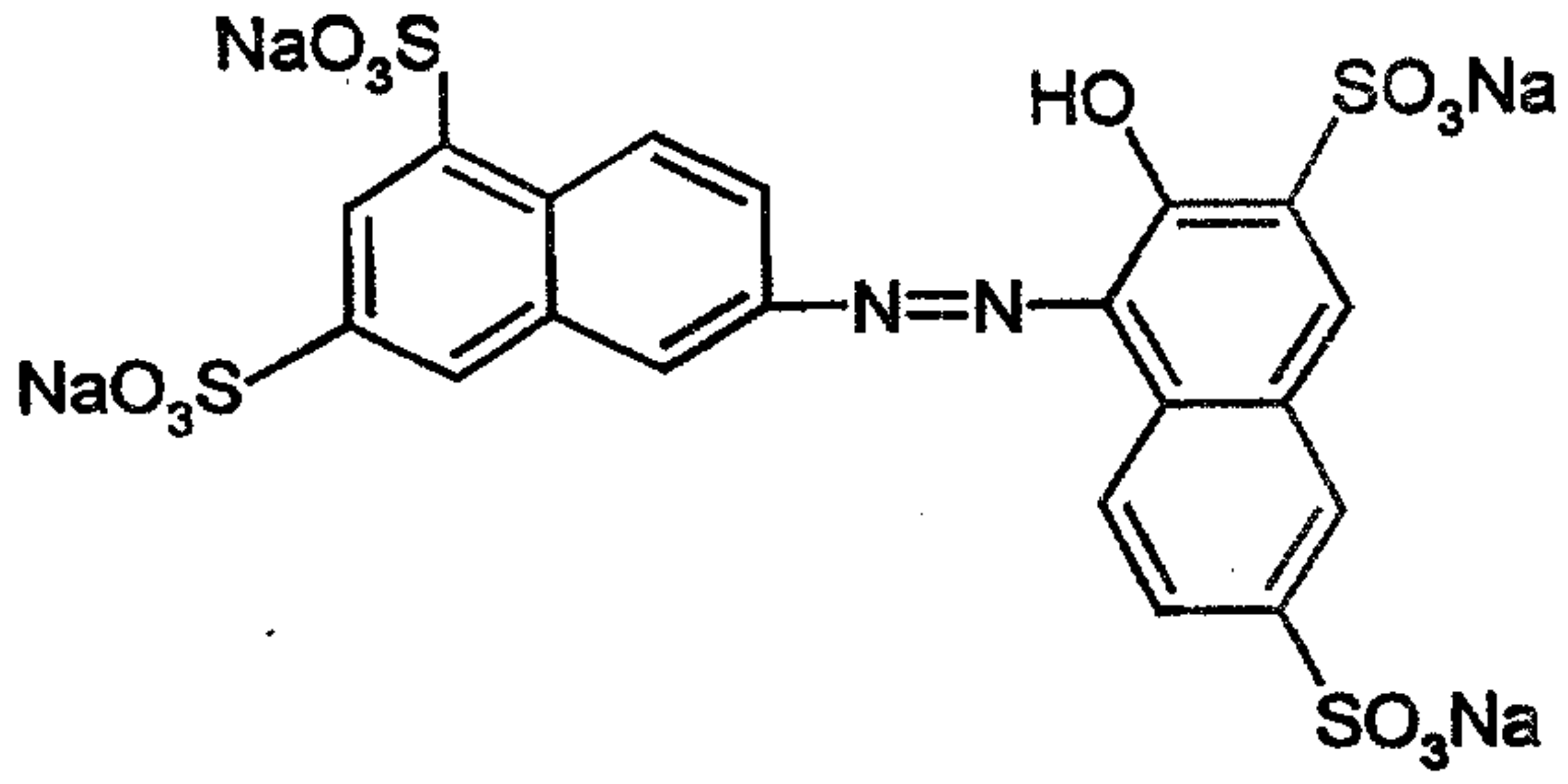


(2)

3 g of the diazonium salt of 2-naphthylamine-6,8-disulfonic acid ("Organikum", 19th edition, p. 560, Verlag Johann Ambrosius Barth Leipzig) are added at 10°C to 120 ml of an aqueous suspension of 2.7 g of 2-naphthylamine-6,8-disulfonic acid and 3 g of sodium acetate, wherein 2 ml of acetic acid are subsequently added dropwise with stirring. After 24 hours' stirring, the product is precipitated with ethanol, removed by suction filtration and dried in a desiccator.

Example 3

Synthesis of 2-hydroxy-1-(naphthyl-2'-azo)-naphthyl-3,6,5',7'-tetrasulfonic acid, tetrasodium salt (3)



(3)

3 g of the diazonium salt of 2-naphthylamine-6,8-disulfonic acid ("Organikum", 19th edition, p. 560, Verlag Johann Ambrosius Barth Leipzig) are added at 10°C to 120 ml of an aqueous suspension of 2.7 g of sodium 2-naphthol-3,6-disulfonate and 3 g of sodium acetate, wherein 2 ml of acetic acid are subsequently added dropwise with stirring. After 24 hours' stirring, the product is precipitated with ethanol, removed by suction filtration and dried in a desiccator.

Example 4:
Reaction of carbon black with azo compounds

The mixture of azo compound and carbon black is produced either by incorporating the carbon black into a solution of the azo compound, subsequently stirring the mixture for 1 hour at room temperature and evaporating the solvent in a drying cabinet (variant 1) or by mixing in a mixer (variant 2). The mixture is then heat-treated for 10 hours at 250°C in a drying cabinet without air circulation, or is irradiated with microwave radiation three times for 1 minute at 700 Watt in a microwave oven. Tables 1a and 1b summarise the examples of the carbon-containing materials with organic groups according to the invention.

Table 1a

No.	Carbon black	Azo compound	Mixture production using variant	Solvent	Reactor
1	FW 18	Naphthol blue black (CI 20470)	1	Water	Drying cabinet
2	FW 18	Naphthol blue black (CI 20470)	2	-	Microwave oven
3	NiPex 160 IQ	Naphthol blue black (CI 20470)	1	Water	Microwave oven
4	NiPex 160 IQ	Naphthol blue black (CI 20470)	2	-	Drying cabinet
5	FW 18	Orange G (CI 16230)	1	Water	Drying cabinet
6	FW 18	Orange G (CI 16230)	2	-	Microwave oven
7	FW 18	Orange G (CI 16230)	1	Water	Microwave oven
8	FW 18	Orange G (CI 16230)	2	-	Drying cabinet
9	FW 18	Methyl orange (CI 13025)	1	Water	Drying cabinet
10	FW 18	Methyl orange (CI 13025)	2	-	Microwave oven
11	FW 18	Methyl orange (CI 13025)	1	Water	Microwave oven
12	FW 18	Methyl orange (CI 13025)	2	-	Drying cabinet
13	FW 18	Hydroxy naphthol blue	1	Water	Drying cabinet
14	FW 18	Hydroxy naphthol blue	2	-	Microwave oven
15	FW 18	Hydroxy naphthol blue	1	Water	Microwave oven
16	FW 18	Hydroxy naphthol blue	2	-	Drying cabinet
17	FW 18	Sulfanil azo chromotrope	1	Water	Drying cabinet
18	FW 18	Sulfanil azo chromotrope	2	-	Microwave oven
19	FW 18	Sulfanil azo chromotrope	1	Water	Microwave oven
20	FW 18	Sulfanil azo chromotrope	2	-	Drying cabinet
21	FW 18	Azobenzene	1	Toluene	Drying cabinet
22	FW 18	Azobenzene	2	-	Microwave oven
23	FW 18	Azobenzene	1	Toluene	Microwave oven
24	FW 18	Azobenzene	2	-	Drying cabinet
25	FW 18	Azobenzene 4-carboxylic acid	1	Water	Drying cabinet
26	FW 18	Azobenzene 4-carboxylic acid	2	-	Microwave oven

Table 1b

No.	Carbon black	Azo compound	Mixture production using variant	Solvent	Reactor
27	FW 18	Azobenzene 4-carboxylic acid	1	Water	Microwave oven
28	FW 18	Azobenzene 4-carboxylic acid	2	–	Drying cabinet
29	Printex 95	4-Sulfonamidoazobenzene[1]	1	Acetone	Drying cabinet
30	Printex 95	4-Sulfonamidoazobenzene[1]	2	–	Microwave oven
31	Printex 95	4-Sulfonamidoazobenzene[1]	1	Acetone	Microwave oven
32	Printex 95	4-Sulfonamidoazobenzene[1]	2	–	Drying cabinet
33	N 220	4-Rhodanoazobenzene[2]	1	Acetone	Drying cabinet
34	N 220	4-Rhodanoazobenzene[2]	2	–	Microwave oven
35	N 220	4-Rhodanoazobenzene[2]	1	Acetone	Microwave oven
36	N 220	4-Rhodanoazobenzene[2]	2	–	Drying cabinet
37	FW 18	Azo compound according to Example 1	1	Water	Drying cabinet
38	FW 18	Azo compound according to Example 1	2	–	Microwave oven
39	NiPex 160 IQ	Azo compound according to Example 1	1	Water	Microwave oven
40	NiPex 160 IQ	Azo compound according to Example 1	2	–	Drying cabinet
41	FW 18	Azo compound according to Example 2	1	Water	Drying cabinet
42	FW 18	Azo compound according to Example 2	2	–	Microwave oven
43	NiPex 160 IQ	Azo compound according to Example 2	1	Water	Microwave oven
44	NiPex 160 IQ	Azo compound according to Example 2	2	–	Drying cabinet
45	FW 18	Azo compound according to Example 3	1	Water	Drying cabinet
46	FW 18	Azo compound according to Example 3	2	–	Microwave oven
47	NiPex 160 IQ	Azo compound according to Example 3	1	Water	Microwave oven
48	NiPex 160 IQ	Azo compound according to Example 3	2	–	Drying cabinet
49	Printex 35	Bis-[4,4'-(diisobutylamino)]azobenzene[3]	1	Toluene	Drying cabinet
50	Printex 35	Bis-[4,4'-(diisobutylamino)]azobenzene[3]	2	–	Microwave oven
51	Printex 35	Bis-[4,4'-(diisobutylamino)]azobenzene[3]	1	Toluene	Microwave oven
52	Printex 35	Bis-[4,4'-(diisobutylamino)]azobenzene[3]	2	–	Drying cabinet

[1] according to Chrzaszczewska et al., Rocz. Chem. 17 (1937) 411

[2] according to Badger et al, J. Chem. Soc. (1953) 2147

[3] according to Lippmann Chem. Ber. 15 (1882) 2163

The carbon blacks FW 18 and NiPex 160 IQ are gas blacks from Degussa AG. The carbon blacks Printex 35, Printex 95 and N 220 are furnace blacks from Degussa AG.

Example 5:

Production and characterisation of dispersions according to the invention

Average particle size and zeta potential are determined by photon correlation spectroscopy (PCS). Zeta potential, which describes the charge state of the particles, provides an indication of the stability of the dispersion.

The instrument used is a Nicomp N370 (Hiac/Royco) photon correlation spectrometer with measurement cells (10 mm disposable measurement cells). Measurement is performed in a 1% AMP 90 solution (prepared with ultrapure water; AMP 90 is a 2-amino-2-methyl-1-propanol solution from Angus Chemie). This solution is initially introduced into the disposable measurement cell and a few drops of sample suspension are added thereto by pipette until an intensity of 300 (± 50) kHz is reached (instrument display at sensitivity 150) or the intensity ceases to rise despite further addition of sample. An excessively high sample concentration should be avoided. Measurement is started in automatic mode. Measurement time is generally 40 minutes. Evaluation is performed by Gaussian analysis (volume distribution). If the value for BASELINE ADJUST is > 1 or the measurement is not yet sufficiently stable (> 5%/10 minutes), the measurement time is extended. The measurement is performed as a duplicate determination. The span of the mean values should be < 10%.

Zeta potential is determined with an MBS-8000 instrument from Matec. The optimum volume concentration for measurement is between 2 and 3 vol.%.

The pH value is determined directly in the carbon black dispersion using a conventional commercial measuring electrode.

Stability testing is performed as follows:

The dispersion is stored for 28 days at room temperature, then frozen to -30°C and heated to 70°C. Viscosity is determined beforehand and afterwards as a measure of stability.

The degree of dispersion is estimated by microscope. To this end, the undiluted dispersion is observed at 400 times magnification under a Nikon light microscope. If no discrete particles are to be observed under these conditions, the dispersion meets requirements with regard to degree of dispersion.

Production of aqueous dispersions

15% of carbon-containing material with organic groups (Example 3, nos. 1-20; 25-28; 37-48) are combined with 0.3% biocide (Acticide MBS from Thor Chemie) and the mixture is made up to 100% with water. A predispersion is prepared therefrom with an Ultra Turrax T50 disperser and dispersing tool. Further processing proceeds in a continuous ultrasound disperser (Dr. Hielscher GmbH, model UIP 500). After dispersion, a pH value of between 7 and 9 is established by addition of base, such as for example AMP 90

(Angus Chemie). Table 2 shows the analytical data for some aqueous dispersions.

Table 2

Dispersion No.	Carbon-containing material with organic groups according to Example 3, no.	Degree of dispersion	Average particle size [nm]	Zeta potential [mV]	Viscosity after 1 day [cPs]	Viscosity after 28 days [cPs]
1	1	*	75	- 52	2.19	2.44
2	7	*	96	- 48	3.97	5.01
3	10	*	81	- 53	2.38	3.22
4	37	*	90	- 40	2.65	2.78
5	48	*	71	- 47	2.42	2.57

*Meets requirements (see above)

Production of solvent-containing dispersions

15-30% of carbon-containing material with organic groups (Example 3, nos. 21-24; 29-36; 49-52) are made up to 100% with solvents, such as toluene, methanol and 2-butoxyethyl acetate. A predispersion is prepared therefrom with an Ultra Turrax T50 disperser and dispersing tool. Further processing proceeds in a continuous ultrasound disperser (Dr. Hielscher GmbH, model UIP 500). Table 3 shows the analytical data for some solvent-containing dispersions.

Table 3

Dispersion No.	Carbon-containing material with organic groups according to Example 3, no.	Solvent	Degree of dispersion
6	21	Toluene	*
7	22	2-Butoxyethyl acetate	*
8	23	Toluene	*
9	24	2-Butoxyethyl acetate	*
10	29	Methanol	*
11	30	2-Butoxyethyl acetate	*
12	31	Methanol	*
13	32	2-Butoxyethyl acetate	*
14	33	Toluene	*
15	34	2-Butoxyethyl acetate	*
16	35	Toluene	*
17	36	2-Butoxyethyl acetate	*
18	49	Toluene	*
19	50	2-Butoxyethyl acetate	*
20	51	Toluene	*
21	52	2-Butoxyethyl acetate	*

*Meets requirements (see above)

Example 6

Applicational tests in aqueous inkjet formulations

Inkjet inks are formulated for test purposes on the basis of the aqueous dispersions according to the invention. To this end, the dispersions are combined with additives and printed with a Hewlett-Packard Deskjet 970 cxi. Printing behaviour and the printed image are evaluated visually and optical density (OD) determined on test prints with a Macbeth RD 918 densitometer. The print results for the inks in Table 4 are based on the dispersions from Table 2.

The constituents of the ink are:

- 5 wt.-% 1,2-propanediol,
- 12 wt.-% 2-pyrrolidone,

- 0.02 wt.-% Surfynol 465 (Air Products),
- 3.0 wt.-% Liponic EG-07 (Permcos GmbH),
- 76 wt.-% deionised water,
- 5 wt.-% carbon-containing material according to the invention with organic groups.

Table 4

Dispersion according to Example 4, no.	Printing behaviour	Printed image	OD Copy paper	OD HP 51634Z	OD Epson 720dpi	OD Canon HR-101	OD Schoeller
1	Fine striping at beginning, then no problem	2	1.48	1.47	1.59	1.46	1.47
2	Fine striping at beginning, then no problem	1	1.49	1.52	1.56	1.54	1.51
3	No problems	1	1.56	1.57	1.61	1.60	1.51
4	No problems	1	1.51	1.57	1.59	1.61	1.53
5	No problems	1	1.56	1.54	1.68	1.64	1.56

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A carbonaceous material with organic groups, obtained by a process comprising:

contacting an organic compound of formula I with a carbonaceous material during the production of said carbonaceous material, wherein said contacting is under conditions that are sufficient to cause a reaction;

$$R^1-N=N-R^2 \qquad (I)$$

wherein R^1 and R^2 are identical or different, and are aryl groups which are unsubstituted or substituted with one or more acceptor substituents or one or more donor substituents; and

wherein the conditions that are sufficient to cause reaction occur within a temperature range of from 250° to 1500°C.

2. A carbonaceous material with organic groups according to claim 1, wherein said one or more acceptor substituents is $-COOR^3$, $-COR^3$, $-CN$, $-SCN$, $-NCS$, $-NCO$, $-NO_2$, $-SO_2R^3$, $-SO_2N(R^3)_2$, $-SO_3R^3$, $-SO_3X$, or $-COOX$, or any combination thereof;

wherein R^3 is identical or different and at each occurrence is H, an alkyl, an aryl, a functionalized alkyl, or a functionalized aryl; and

wherein X is H, an alkali metal ion, or an ammonium ion.

3. A carbonaceous material with organic groups according to claim 1 or 2, wherein said one or more donor substituents is an alkyl group, an aryl group, OR^4, $N(R^4)_2$, SR^4, $-S-S-R^4$, or $P(R^4)_2$, or any combination thereof;

wherein R^4 is identical or different and at each occurrence is H, an alkyl, an aryl, a functionalized alkyl, or a functionalized aryl.

4. A carbonaceous material with organic groups according to claim 1, 2 or 3, wherein the contacting of the organic compound of formula I to the carbonaceous material occurs as a powder, melt or solution.

5. A carbonaceous material with organic groups according to any one of claims 1 to 3, wherein the contacting occurs in the absence of a solvent.

6. A carbonaceous material with organic groups according to any one of claims 1 to 3, wherein the contacting occurs in the presence of a solvent.

7. A carbonaceous material with organic groups according to any one of claims 1 to 6, wherein the ratio of the carbonaceous material to the organic compound of formula I ranges from 99.99:0.01 to 0.01:99.99.

8. A carbonaceous material with organic groups according to any one of claims 1 to 6, wherein the ratio of the

carbonaceous material to the organic compound of formula I ranges from 50:1 to 1:50.

9. A process for the production of a carbonaceous material with organic groups comprising:

contacting an organic compound of formula I with a carbanaceous material during the production of said carbonaceous material, wherein said contacting is under conditions that are sufficient to cause a reaction;

$$R^1\text{—}N\text{=}N\text{—}R^2 \qquad (I)$$

wherein R^1 and R^2 are identical or different, and are aryl groups which are unsubstituted or substituted with one or more acceptor substituents or one or more donor substituents; and

wherein the conditions that are sufficient to cause reaction occur within a temperature range of from 250° to 1500° C.

10. A process for the production of the carbonaceous material with organic groups according to claim 9, wherein the contacting of the organic compound of formula I to the carbonaceous material occurs as a powder, melt or solution.

11. A process for the production of the carbonaceous material with organic groups according to claim 9 or 10, wherein the contacting occurs in the absence of a solvent.

12. A process for the production of the carbonaceous material with organic groups according to claim 9 or 10, wherein the contacting occurs in the presence of a solvent.

13. A process for the production of the carbonaceous material with organic groups according to any one of claims 9 to 12, wherein the ratio of the carbonaceous material to the organic compound of formula I ranges from 99.99:0.01 to 0.01:99.99.

14. A process for the production of the carbonaceous material with organic groups according to any one of claims 9 to 12, wherein the ratio of the carbonaceous material to the organic compound of formula I ranges from 50:1 to 1:50.

15. A composition, comprising:
a carbonaceous material with organic groups as defined in any one of claims 1 to 8, and a carrier.

16. A composition according to claim 15, wherein the carrier is rubber, plastic, ink, toner, lacquer, paint, paper, bitumen, or concrete.

17. A composition according to claim 16, wherein the ink is printing ink or inkjet ink.

18. A dispersion, comprising:
a carbonaceous material with organic groups as defined in any one of claims 1 to 8, and an additive.

19. A dispersion according to claim 18, wherein the additive is a monomeric compound, an oligomeric compound, or a polymeric compound.

20. A tire, comprising:

a carbonaceous material with organic groups as defined in any one of claims 1 to 8, and a rubber.

21. A filled composition, comprising:

a matrix material containing the carbonaceous material with organic groups as defined in any one of claims 1 to 8;

wherein the matrix material is paper, plastic, metal, glass, a polymer, a fiber, leather, wood, concrete, or rubber.

22. A carbonaceous material with organic groups, obtained by a process comprising:

contacting an organic compound of formula I with a carbonaceous material under conditions that are sufficient to cause a reaction;

$$R^1\text{–N=N–}R^2 \qquad (I)$$

wherein R^1 and R^2 are identical or different, and are aryl groups which are unsubstituted or substituted with one or more acceptor substituents or one or more donor substituents;

wherein the ratio of the carbonaceous material to the organic compound of formula I ranges from 99.99:0.01 to 0.01:99.99; and

wherein the conditions that are sufficient to cause a reaction occur within a temperature range of from -80° to 300°C.

23. A carbonaceous material with organic groups according to claim 22, wherein said contacting occurs during production of the carbonaceous material, and wherein said conditions that are sufficient to cause reaction occurs within a temperature range of from 250° to 1500°C.

24. A carbonaceous material with organic groups according to claim 22, wherein said one or more acceptor substituents is $-COOR^3$, $-COR^3$, $-CN$, $-SCN$, $-NCS$, $-NCO$, $-NO_2$, $-SO_2R^3$, $-SO_2N(R^3)_2$, $-SO_3R^3$, $-SO_3X$, or $-COOX$, or any combination thereof;

wherein R^3 is identical or different, and at each occurrence is H, an alkyl, an aryl, a functionalized alkyl, or a functionalized aryl; and

wherein X is H, an alkali metal ion, or an ammonium ion.

25. A carbonaceous material with organic groups according to claim 22, wherein said one or more donor substituents is an alkyl group, an aryl group, OR^4, $N(R^4)_2$, SR^4, $-S-S-R^4$, or $P(R^4)_2$, or any combination thereof;

wherein R^4 is identical or different, and at each occurrence is H, an alkyl, an aryl, a functionalized alkyl, or a functionalized aryl.

26. A carbonaceous material with organic groups according to any one of claims 22 to 25, wherein the contacting of the organic compound of formula I to the carbonaceous material occurs as a powder, melt or solution.

27. A carbonaceous material with organic groups according to any one of claims 22 to 25, wherein the contacting occurs in the absence of a solvent.

28. A carbonaceous material with organic groups according to any one of claims 22 to 25, wherein the contacting occurs in the presence of a solvent.

29. A carbonaceous material with organic groups according to any one of claims 22 to 28, wherein the ratio of the carbonaceous material to the organic compound of formula I ranges from 50:1 to 1:50.

30. A dispersion, comprising:

the carbonaceous material with organic groups as defined in any one of claims 22 to 29, and an additive.

31. A dispersion according to claim 30, wherein the additive is a monomeric compound, an oligomeric compound, or a polymeric compound.

32. A tire, comprising:

the carbonaceous material with organic groups as defined in any one of claims 22 to 29, and a rubber.

33. A filled composition, comprising:

a matrix material containing the carbonaceous material with organic groups as defined in any one of claims 22 to 29;

wherein the matrix material is paper, plastic, metal, glass, a polymer, a fiber, leather, wood, concrete, or rubber.

34. A process for the production of the carbonaceous material with organic groups comprising:

contacting an organic compound of formula I with a carbonaceous material under conditions that are sufficient to pause a reaction;

$$R^1{-}N{=}N{-}R^2 \qquad (I)$$

wherein R^1 and R^2 are identical or different, and are aryl groups which are unsubstituted or substituted with one or more acceptor substituents or one or more donor substituents;

wherein the ratio of the carbonaceous material to the organic compound of formula I ranges from 99.99:0.01 to 0.01:99.99; and

wherein the conditions that are sufficient to cause a reaction occur within a temperature range of from -80° to 300°C.

35. A process for the production of the carbonaceous material with organic groups according to claim 34, wherein said contacting occurs during production of the carbonaceous material, and wherein the conditions that are sufficient to cause a reaction occur within a temperature range of from 250° to 1500°C.

36. A process for the production of the carbonaceous material with organic groups according to claim 34 or 35, wherein the contacting of the organic compound of formula I to the carbonaceous material occurs as a powder, melt or solution.

37. A process for the production of the carbonaceous material with organic groups according to claim 34 or 35, wherein the contacting occurs in the absence of a solvent.

38. A process for the production of the carbonaceous material with organic groups according to claim 34 or 35, wherein the contacting occurs in the presence of a solvent.

39. A process for the production of the carbonaceous material with organic groups according to claim 34 or 35, wherein the ratio of the carbonaceous material to the organic compound of formula I ranges from 50:1 to 1:50.

40. A composition, comprising:

the carbonaceous material with organic groups as defined in any one of claims 22 to 29, and a carrier.

41. A composition according to claim 40, wherein the carrier is rubber, plastic, ink, toner, lacquer, paint, paper, bitumen, or concrete.

42. A composition according to claim 41, wherein the ink is printing ink or inkjet ink.