



(86) Date de dépôt PCT/PCT Filing Date: 2004/12/30  
(87) Date publication PCT/PCT Publication Date: 2005/08/04  
(45) Date de délivrance/Issue Date: 2013/03/26  
(85) Entrée phase nationale/National Entry: 2006/07/14  
(86) N° demande PCT/PCT Application No.: US 2004/044025  
(87) N° publication PCT/PCT Publication No.: 2005/071017  
(30) Priorité/Priority: 2004/01/14 (US10/757,306)

(51) Cl.Int./Int.Cl. *C09B 48/00* (2006.01)  
(72) Inventeurs/Inventors:  
SUNG, EDWARD H., US;  
DONG, JAMES Z., US;  
ROBERTSON, GEORGE H., US  
(73) Propriétaire/Owner:  
SUN CHEMICAL CORPORATION, US  
(74) Agent: MCCARTHY TETRAULT LLP

(54) Titre : PREPARATION DE QUINACRIDONEQUINONES ET DERIVES SUBSTITUES DE CELLES-CI  
(54) Title: PREPARATION OF QUINACRIDONEQUINONES AND SUBSTITUTED DERIVATIVES OF SAME

(57) **Abrégé/Abstract:**

A process for oxidizing a quinacridone in a liquid medium with a non-metal oxidant to produce a quinacridonequinone.

## (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
4 August 2005 (04.08.2005)

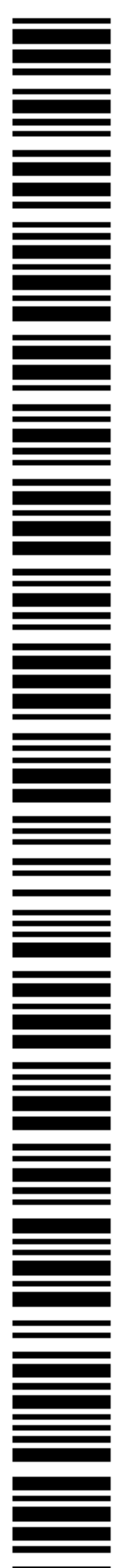
PCT

(10) International Publication Number  
**WO 2005/071017 A1**

- (51) International Patent Classification<sup>7</sup>: **C09B 48/00**
- (21) International Application Number:  
PCT/US2004/044025
- (22) International Filing Date:  
30 December 2004 (30.12.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
10/757,306 14 January 2004 (14.01.2004) US
- (71) Applicant (for all designated States except US): **SUN CHEMICAL CORPORATION** [US/US]; 222 Bridge Plaza South, Fort Lee, NJ 07024 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **SUNG, Edward, H.** [US/US]; 10803 Stockbridge Lane, Cincinnati, OH 45249 (US). **DONG, James, Z.** [CN/US]; 7769 W. Bay Drive, Mason, OH 45040 (US). **ROBERTSON, George, H.** [GB/US]; 9177 Pinewood Drive, Loveland, OH 45140 (US).
- (74) Agent: **PERSLEY, Sidney**; 222 Bridge Plaza South, Fort Lee, NJ 07024 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
- with international search report
  - before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: PREPARATION OF QUINACRIDONEQUINONES AND SUBSTITUTED DERIVATIVES OF SAME

(57) Abstract: A process for oxidizing a quinacridone in a liquid medium with a non-metal oxidant to produce a quinacridonequinone.



**WO 2005/071017 A1**

5                   **PREPARATION OF QUINACRIDONEQUINONES AND SUBSTITUTED  
                          DERIVATIVES OF SAME**

**BACKGROUND OF THE INVENTION**

10 [0001] The invention relates to a process for the preparation of quinacridonequinone pigments and substituted derivatives.

**DESCRIPTION OF THE RELATED ART**

15 [0002] Quinacridonequinone and its various derivatives are well known compounds which are used in the manufacture of commercial pigments. In recent years, developments have led quinacridonequinone pigments which are of great importance with respect to their light and weathering fastness and color properties. For example, U.S. Patent 4,693,753 discloses the formation quinacridonequinone pigments and derivates of same.

20 [0003] Quinacridonequinone and its substituted derivatives have been prepared by various processes. As described in U.S. Patent 3,185,694, a quinacridonequinone pigment can be made by the condensation of anthranilic acid with benzoquinones in the presence of suitable oxidizing agents, followed by cyclization under the influence of dehydrating agents such as concentrated sulfuric acid. Quinacridonequinone pigments  
25 can also be prepared by the oxidation of quinacridones with sodium dichromate or potassium permanganate as described in U.S. Patent 3,632,588 or by the oxidation of corresponding dihydroquinacridones as described in U.S. Patent 3,251,845 in which dihydroquinacridone is heated in a medium containing dichromate or permanganate. Although the quinacridonequinones produced according to U.S. Patent 3,251,845 are  
30 highly satisfactory for many pigmentary applications, the purity and intensity of color are not as high as desirable, especially for high quality pigmentary applications. Furthermore, the oxidation reaction in the all of these patents produce relatively large concentrations of heavy metal ions which must be removed from the reaction medium to avoid environmental pollution upon disposal of the reaction medium.

35 [0004] Other oxidations using non-heavy metal have been reported. As described in U.S. Patent 4,025,518, a quinacridonequinone is prepared by the oxidation of dihydroquinacridone in an aqueous acidic medium using an alkali metal chlorate as the oxidizing agent in the presence of vanadium pentoxide and, optionally, passing air

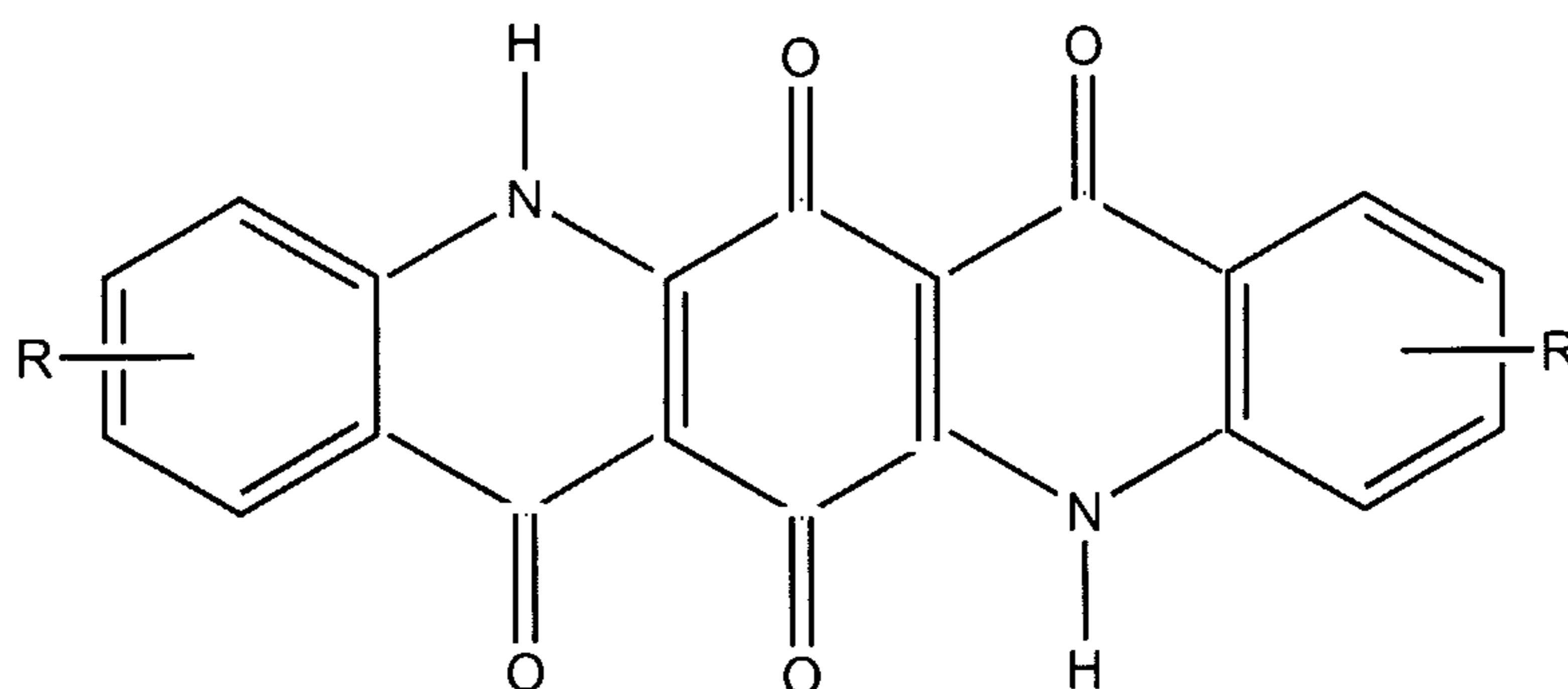
5 through the aqueous acidic medium during the oxidation. This process is cumbersome and expensive.

[0005] Thus, a need exists for a simpler, less expensive and/or more environmentally friendly process for producing a high quality quinacridonequinone composition having increased purity and color strength.

10

### SUMMARY OF THE INVENTION

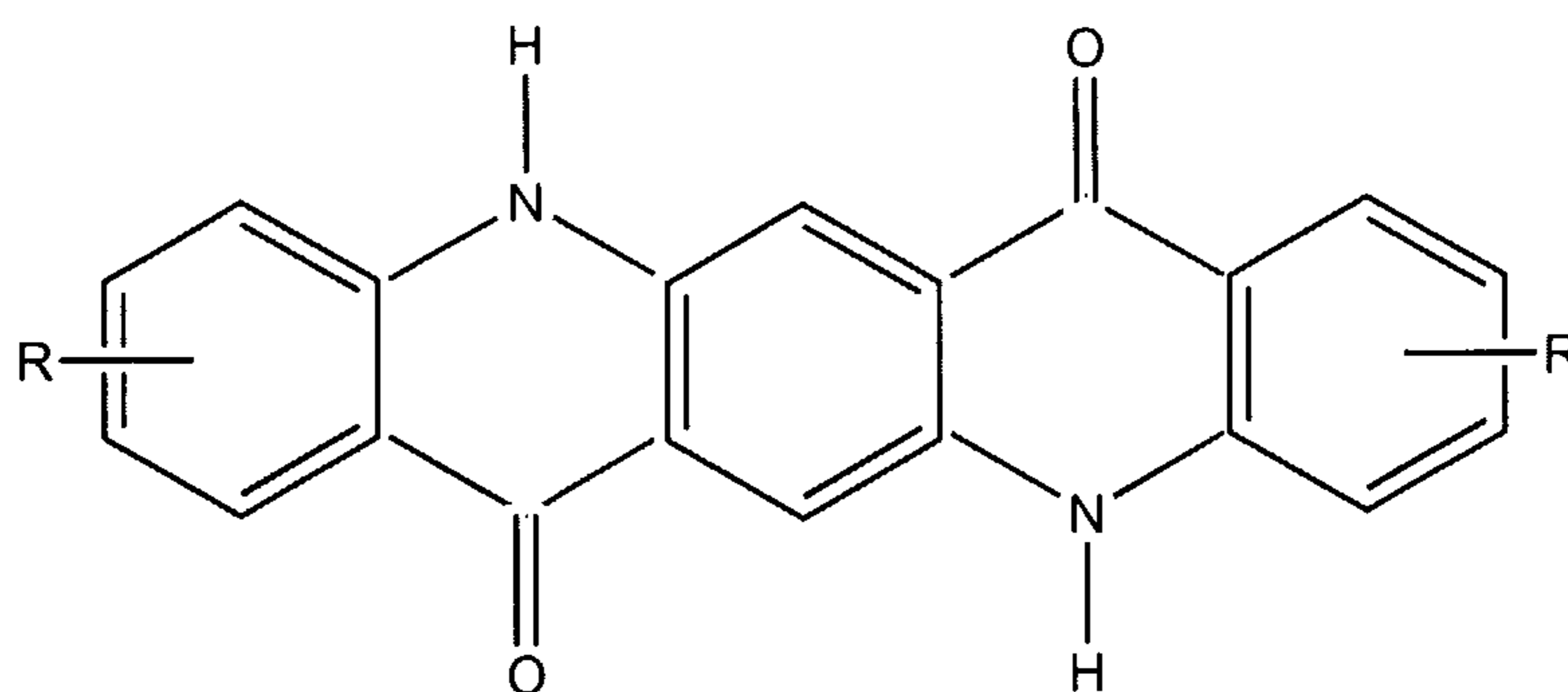
[0006] It has now been found that the above objectives can be realized by employing a process for preparing a quinacridonequinone of the formula



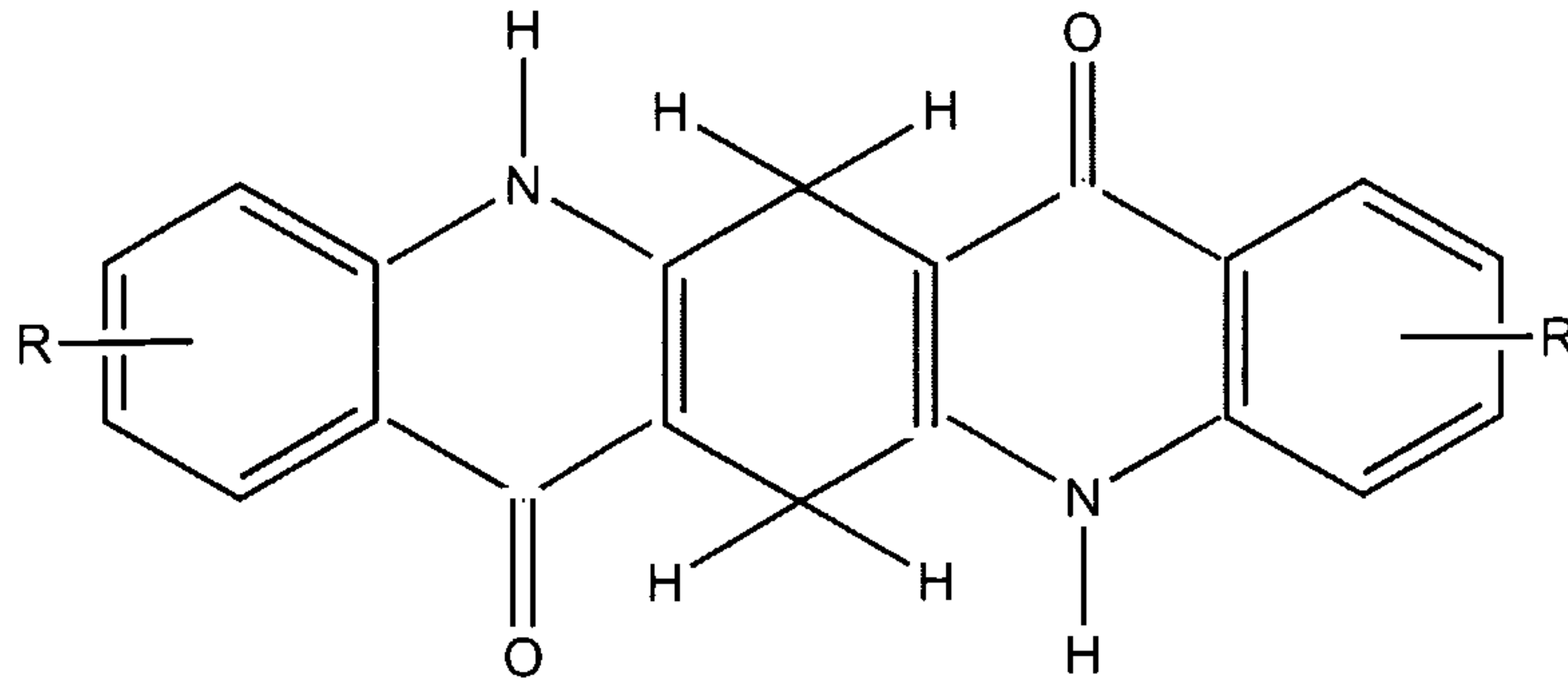
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wherein R is hydrogen, a halogen, a C<sub>1</sub>-C<sub>10</sub>-alkoxy, a C<sub>1</sub>-C<sub>10</sub>-alkyl or a substituted or unsubstituted phenyl, by oxidizing the quinacridone in a liquid medium with a non-metal oxidant, with the quinacridone being of the formula:

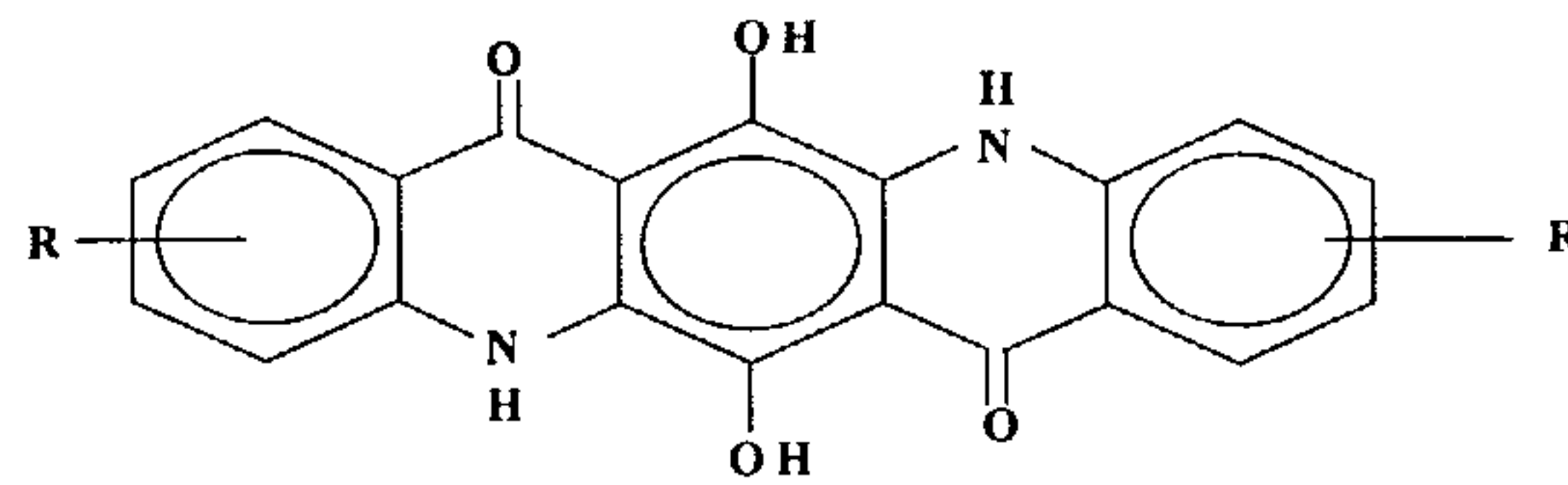
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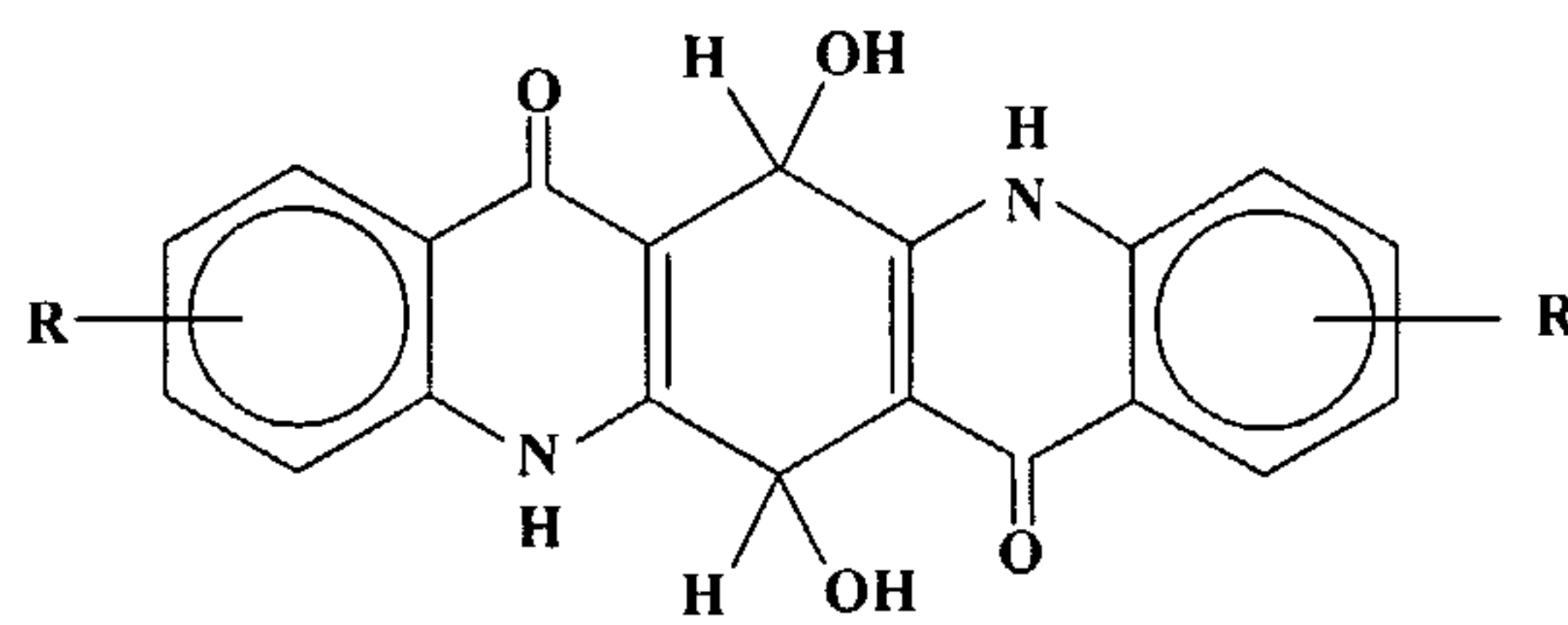
or



or



or



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[0007] The present invention further provides a method for increasing the purity of a quinacridonequinone when prepared by the process as described above.

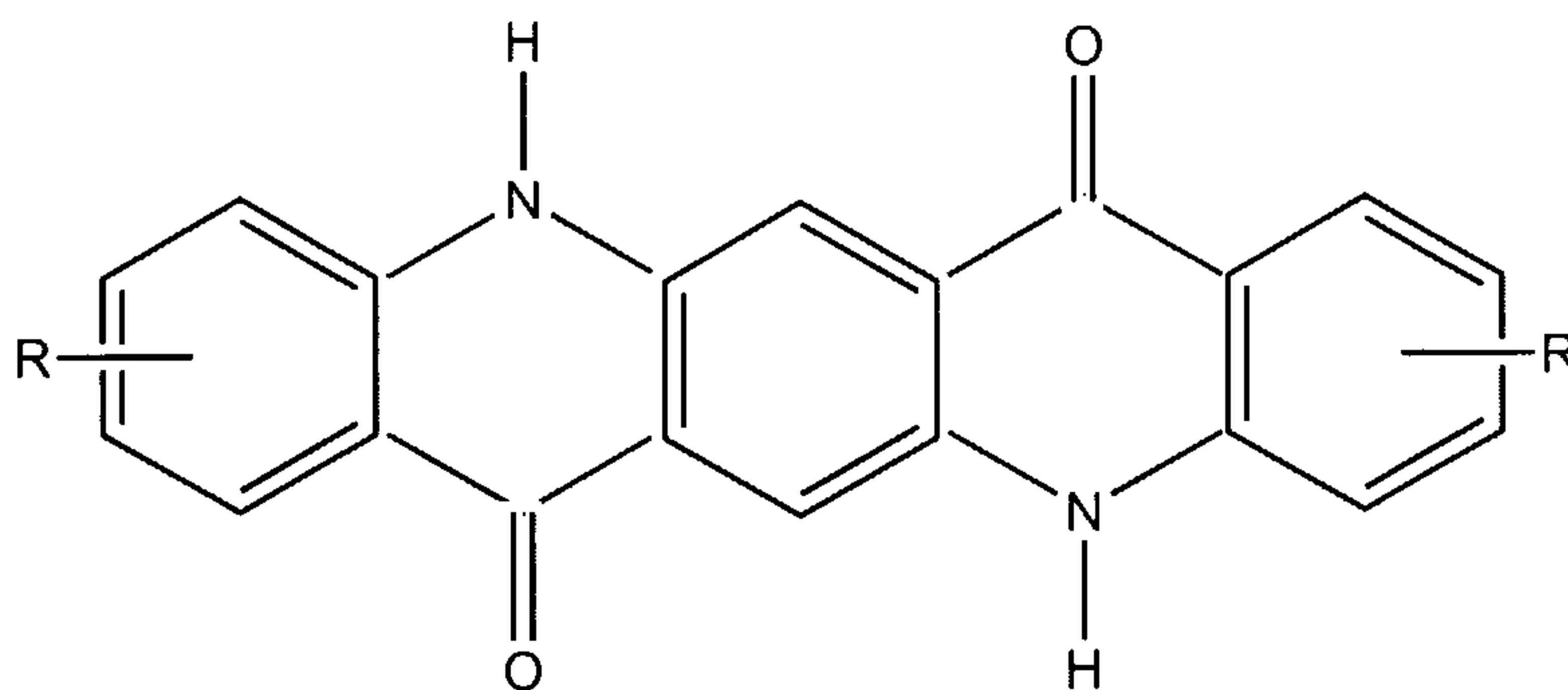
[0008] Other objects and advantages of the present invention will become apparent from the following description and appended claims.

### DETAILED DESCRIPTION OF THE INVENTION

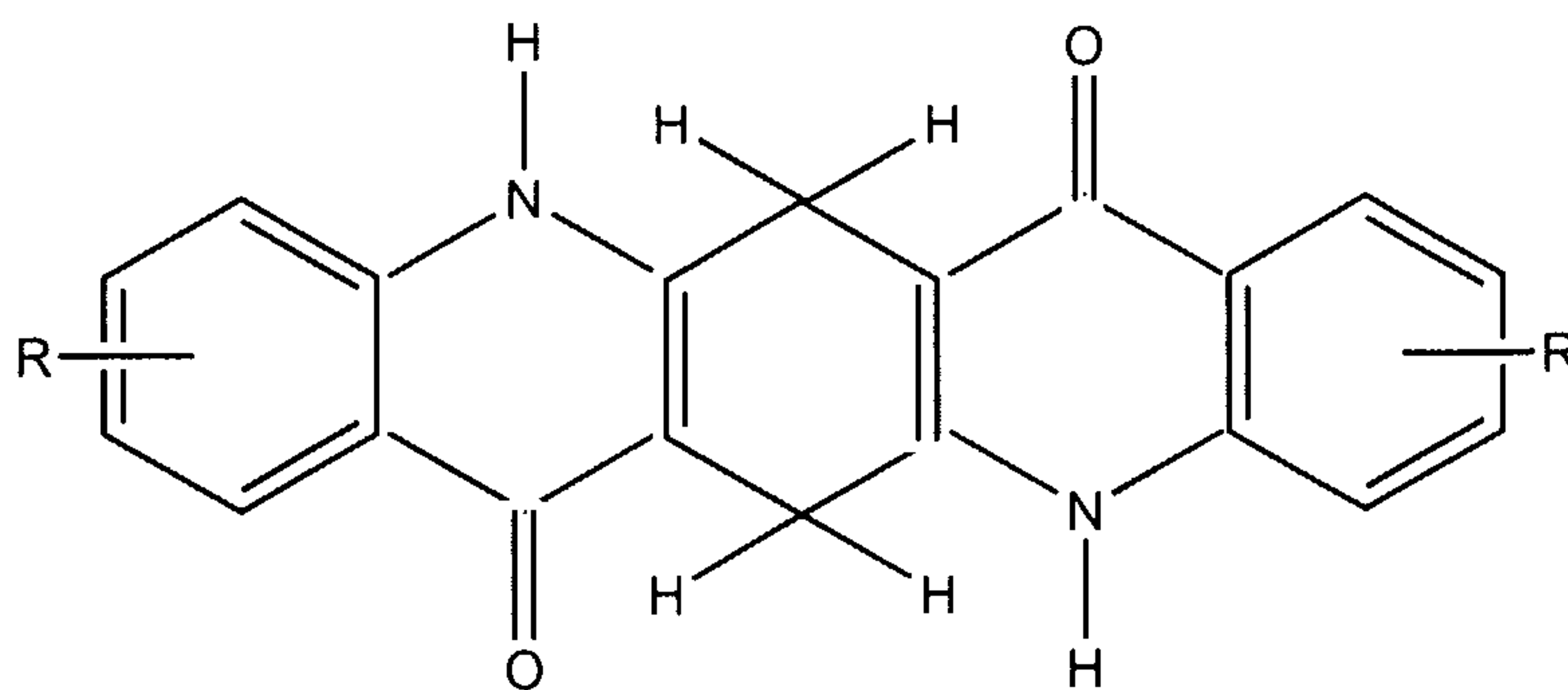
10 [0009] Quinacridonequinones having increased purity are prepared by oxidizing quinacridones or derivatives of same with a non-metal oxidant in a liquid medium, optionally, at elevated temperature.

[0010] The quinacridones utilized in the process of this invention are well known compounds and can be prepared by any of a number of methods known in the art.

15 These methods can be used to produce conventional quinacridone and derivatives of same, including but not limited to quinacridonea, dihydroquinacridonea, dihydroxyquinacridonea and the like. Since a dihydroquinacridone may be considered to be a di-hydrogenated derivative of the corresponding quinacridone, hereafter the term "quinacridone" is to be understood to refer to either the quinacridone or its  
20 dihydroquinacridone derivative. The preferred quinacridones used in the present invention include Formulas I – IV below.

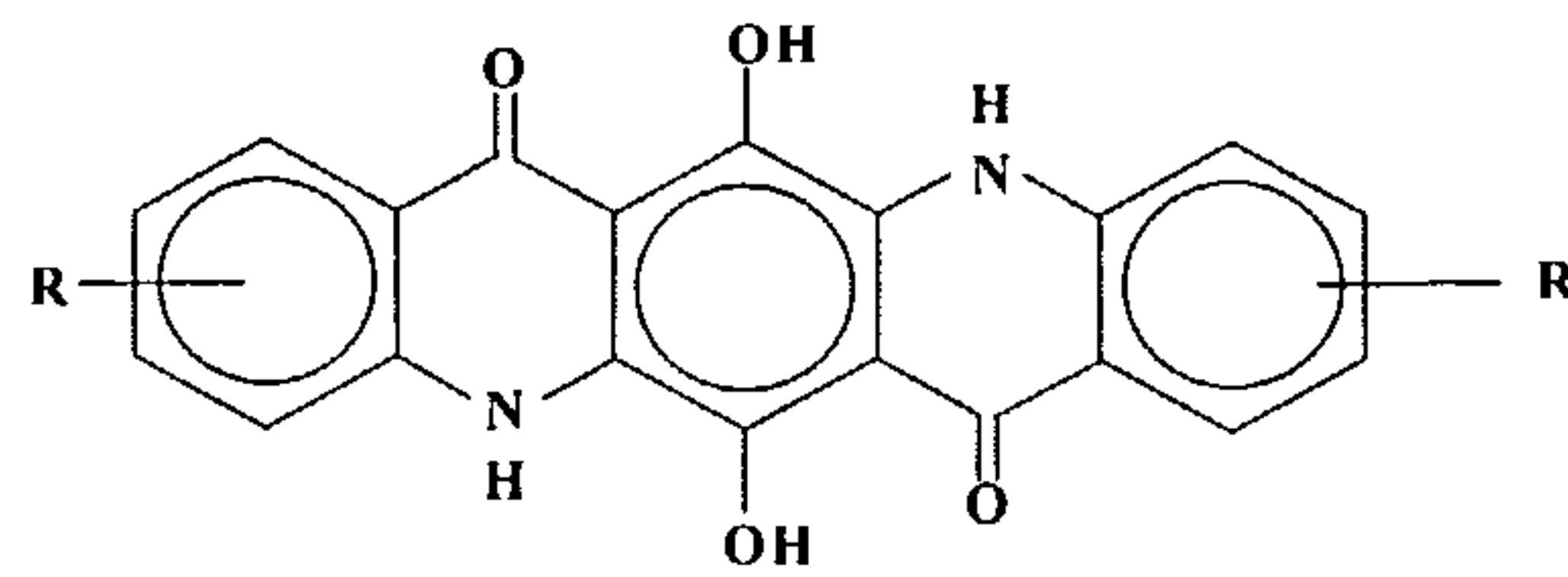


Formula I



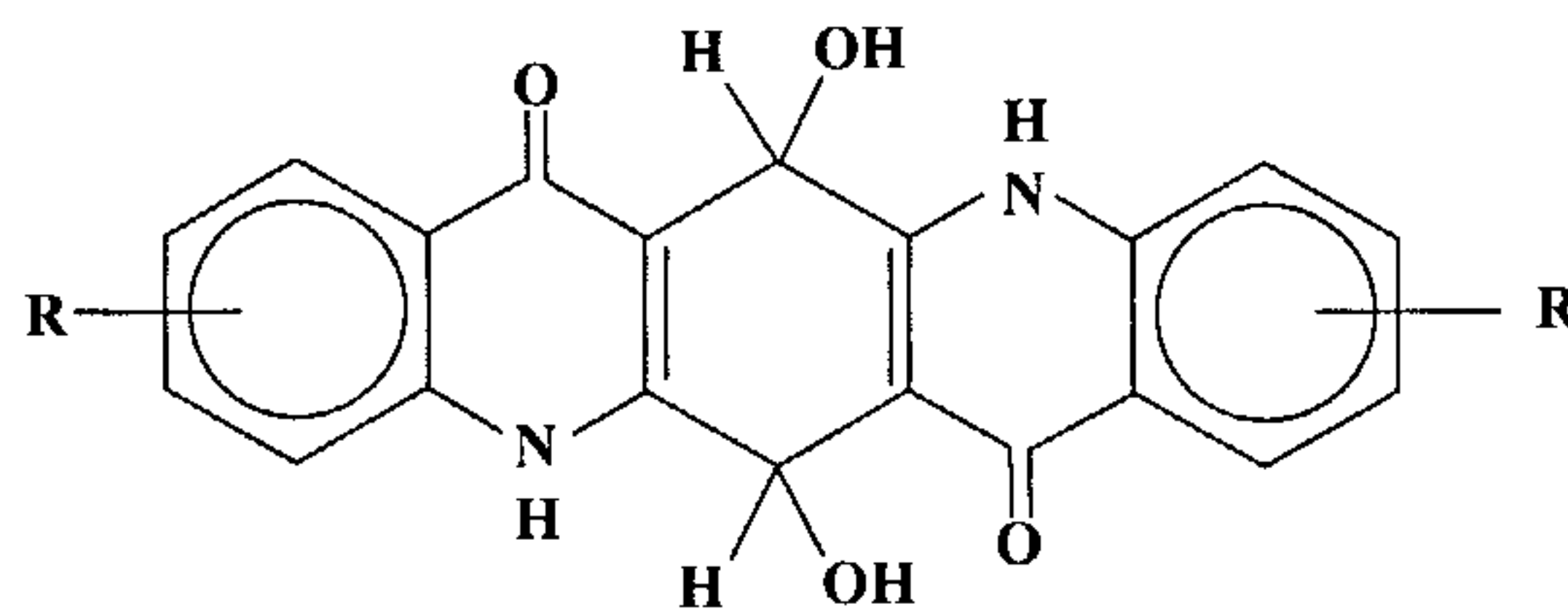
Formula II

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Formula III

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Formula IV

[0011] The liquid medium in which the oxidation is conducted may be water, organic solvents, inorganic solvents and combinations thereof. The organic solvents include but are not limited to dichlorobenzene, trichlorobenzene, and the like and combinations thereof. The inorganic solvents include but are not limited to sulfuric acid, polyphosphoric acid, phosphoric acid, acetic acid, and the like and combinations thereof. When an aqueous medium is utilized, the oxidation reaction can be performed in a neutral, acidic or alkaline condition. Further, a liquid medium may be present during the conventional synthesis process such as the synthesis of quinacridone with water.

5 The main criteria governing the selection of the liquid medium are that the quinacridone can be easily oxidized and that it should not interfere with the oxidation reaction.

[0012] Suitable non-metal oxidants for use in the invention include, but are not limited to, persulfuric acid and the like, persulfuric acid salts and the like such as peroxydosulfuric acid and its salts, sodium peroxydisulfate ( $\text{Na}_2\text{SO}_5$ ), and persulfuric acid derivatives. It is  
10 preferred that the non-metal oxidant be sodium peroxydisulfate ( $\text{Na}_2\text{SO}_5$ ), potassium peroxydisulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), ammonium peroxydisulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ), and the like and combinations thereof. The most preferred non-metal oxidant is sodium peroxydisulfate as it is economical, safety and readily available.

[0013] The quinacridone is oxidized by combining it with a liquid medium and a non-  
15 metal oxidant. The non-metal oxidant should be added at least slightly in excess with respect to the mole ratio of the quinacridone in order to produce the corresponding quinacridonequinone.

[0014] The non-metal oxidants can be added to the liquid reaction medium at many process points depending on the convenience of plant arrangement. The non-metal  
20 oxidants can also be added during the quinacridone synthesis process directly to an aqueous pigment slurry made from pre-isolated quinacridone presscake.

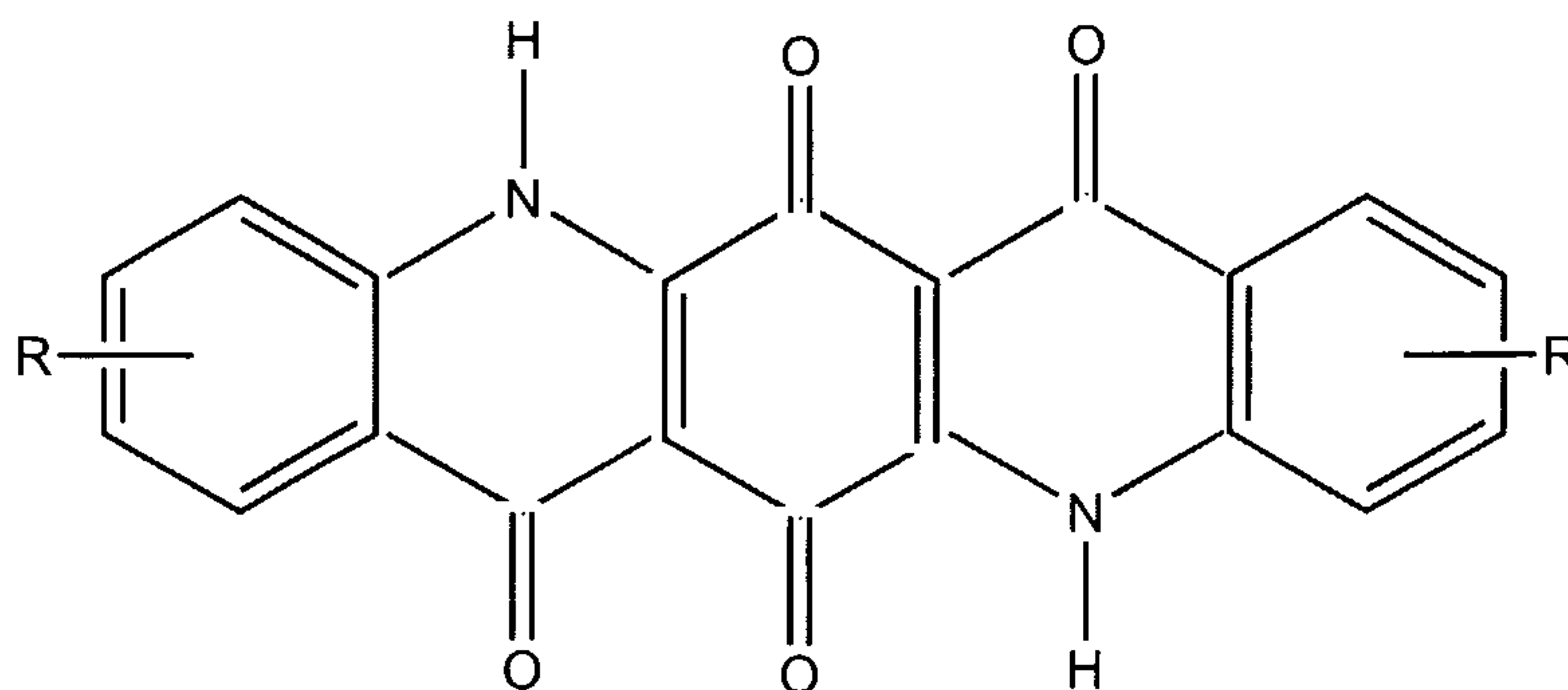
[0015] The oxidation can be conducted at a temperature from room temperature to about  $85^\circ\text{C}$ . The oxidation reaction proceeds less favorably at temperature below  $40^\circ\text{C}$  and results in a poorer quality quinacridonequinone due to incomplete oxidation as the  
25 non-metal oxidants are reasonably stable when cool resulting in a slower decomposition to acid and oxygen. At a temperature higher than  $85^\circ\text{C}$ , oxygen gas evolves quickly from the non-metal oxidant and requires excess non-metal oxidant for a complete reaction, which would increase the cost of production. The preferred temperature for producing quinacridonequinone is between about  $55^\circ\text{C}$  and about  $65^\circ\text{C}$ . The non-metal  
30 oxidant, when heated at a temperature of between about  $40^\circ\text{C}$  to about  $85^\circ\text{C}$ , thus decompose rapidly in strongly acidic solutions, usually to hydrogen peroxide and sulfuric acid depending on the non-metal oxidant chosen.

[0016] Small amounts of iron can be added to catalyze the reaction, such as  $\text{FeSO}$ .

[0017] The quinacridonequinone produced is finished in a conventional manner, e.g.,  
35 filtration, washing and drying. It provides an attractive golden color, useful in metallic finishes with aluminum and can be used to form many solid solutions for coating applications.

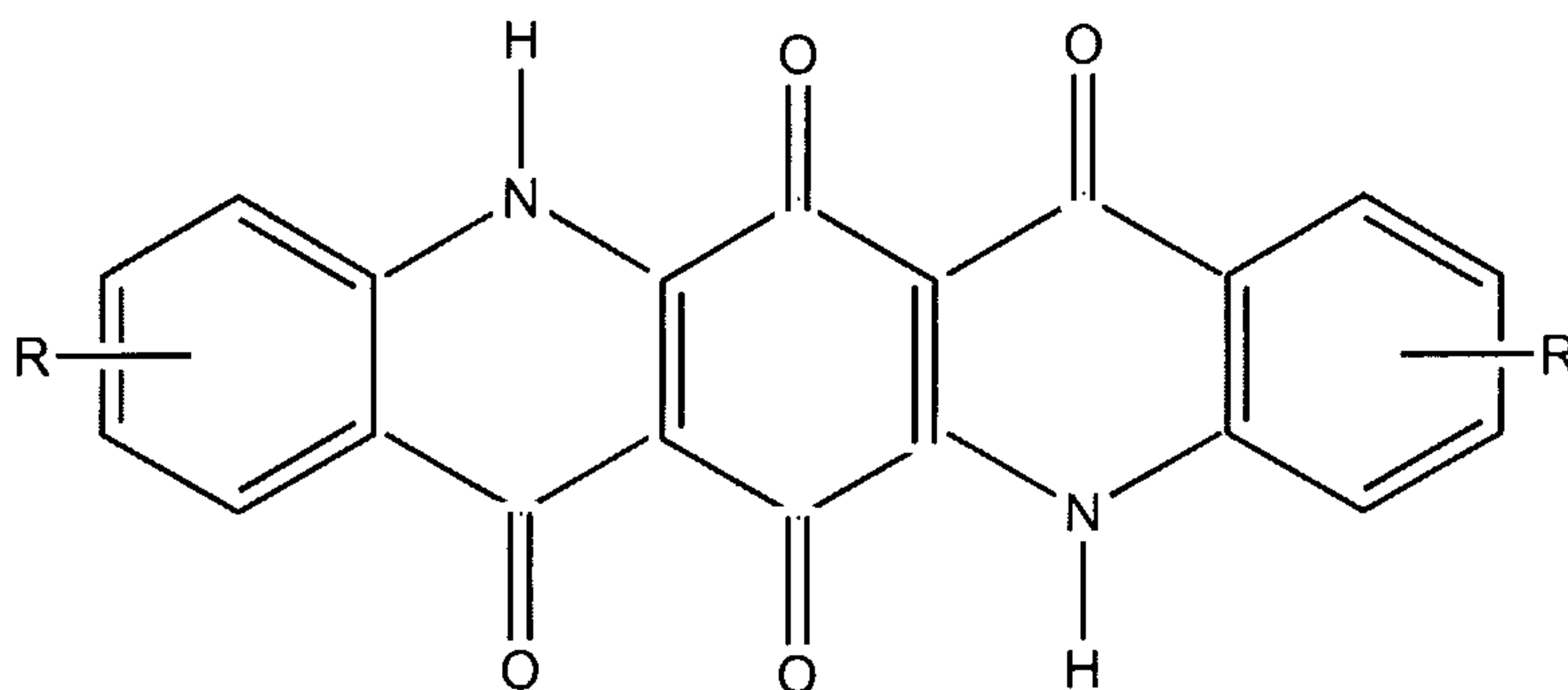
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[0018] The process produces a quinacridonequinone of Formula IV below.



Formula V

10 wherein R is hydrogen, a halogen, a C<sub>1</sub>-C<sub>10</sub>-alkoxy, a C<sub>1</sub>-C<sub>10</sub>-alkyl or a substituted or unsubstituted phenyl. When the oxidation includes a persulfuric acid and/or persulfuric acid salt, the resulting quinacridonequinone is represented by formula VI below.



Formula VI

15 wherein R is as described for formulas I-IV above. Groups exemplary of R are, hydrogen; halogen such as chlorine, bromine; alkoxy such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec-butoxy, pentyloxy, isopentyloxy, neopentyloxy, hexyloxy, isohexyloxy, heptyloxy, octyloxy, 2-ethylhexyloxy, nonyloxy or decyloxy; alkyls such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl,  
 20 pentyl, isopentyl, neopentyl, hexyl, isohexyl, heptyl, octyl, 2-ethylhexyl, nonyl, decyl; phenyl; substituted phenyls such as such as 4-methylphenyl, 2,4- or 2,6-dimethylphenyl, 2-ethylphenyl, 4-ethylphenyl, 4-propylphenyl, 4-isopropylphenyl, 4-butylphenyl, 2-methoxyphenyl, 4-methoxyphenyl, 4-ethoxyphenyl, 4-propoxyphenyl, 4-butoxyphenyl, 2-

5 chlorophenyl, 4-chlorophenyl, 2,4- or 2,6-dichlorophenyl, 4-bromophenyl or 2-methyl-4-chlorophenyl.

[0019] By carrying out the process of the present invention, a quinacridonequinone having a purity of 90% can be achieved as it is believed, while not being bound by theory, that the oxidation process is nearly completed. The purity may be as high as  
10 98%.

[0020] The quinacridonequinone and its method of preparation of the present invention are further illustrated by the following non-limiting examples in which all parts and percentages are by weight, unless otherwise indicated.

15 **EXAMPLE 1**

[0021] Quinacridone (100 grams) was dissolved in concentrated sulfuric acid (500 grams), reacted and then an iron salt (0.1 grams;  $\text{FeSO}_4$ ) was added and the mixture slowly heated to 50°C. Sodium peroxydisulfate (100 grams) was added over a four-hour period, the mixture stirred for an additional two hours and then it was added to  
20 water (2000 grams). After three hours stirring, the slurry was filtered and the presscake washed with water to pH 6.5-7.5 and dried, producing 109 grams of a bright yellow highly pure quinacridonequinone.

**EXAMPLE 2**

[0022] Quinacridone (50 grams) was dispersed in water (1000 grams) and potassium  
25 hydroxide (50 grams) was added. The slurry was heated to 65° C and sodium peroxydisulfate (200 grams) was added over a six-hour period. The slurry was stirred continuously for an additional 8 hours at 65°C and filtered. The resulting presscake was washed with water to neutral and dried, producing 55 grams of bright yellow highly pure quinacridonequinone.

30 **EXAMPLE 3**

[0023] A quinacridone in a liquid medium was prepared by heating polyphosphoric acid (117%; 800 grams) to 115° C and adding dianilinoterephthalic acid (200 grams) over a period of three hours at about 115-120°C. The mixture was further maintained at 115-120°C for one hour and cooled down to 100°C. Water (15 grams) was slowly added  
35 over ten minutes with the temperature maintained at 100-105°C hours and then cooled to 80°C. To the quinacridone in liquid medium was added sodium peroxydisulfate (300 grams) over a four-hour period. The mixture was stirred at 80°C for two hours and then added to water (2000 grams). After three hours stirring, the slurry was filtered and the

5 presscake washed with water to pH 6.5-7.5 and dried , producing 199 grams of a bright yellow highly pure quinacridonequinone.

#### EXAMPLE 4

10 [0024] A quinacridone in a liquid medium was prepared by heating polyphosphoric acid (117%;800 grams) to 115°C and adding dianihino-dihydro-terephthahic acid (200 grams) over a period of three hours at about 115-120°C, then maintained at this temperature for 1 hour, and later cooled down to 100°C. Water (15 grams) was added slowly and temperature maintained at 100-105°C. The quinacridone in liquid medium was added to separate water (1 liter) and then sodium peroxydisulfate (350 grams) was  
15 added slowly over a four hour period at temperature between 40-50° C. After an additional three hours of stirring, the slurry was filtered and the presscake washed with water to pH 6.5-7.51 and dried, producing 198 grams of bright yellow highly pure quinacridonequinone.

#### EXAMPLE 5

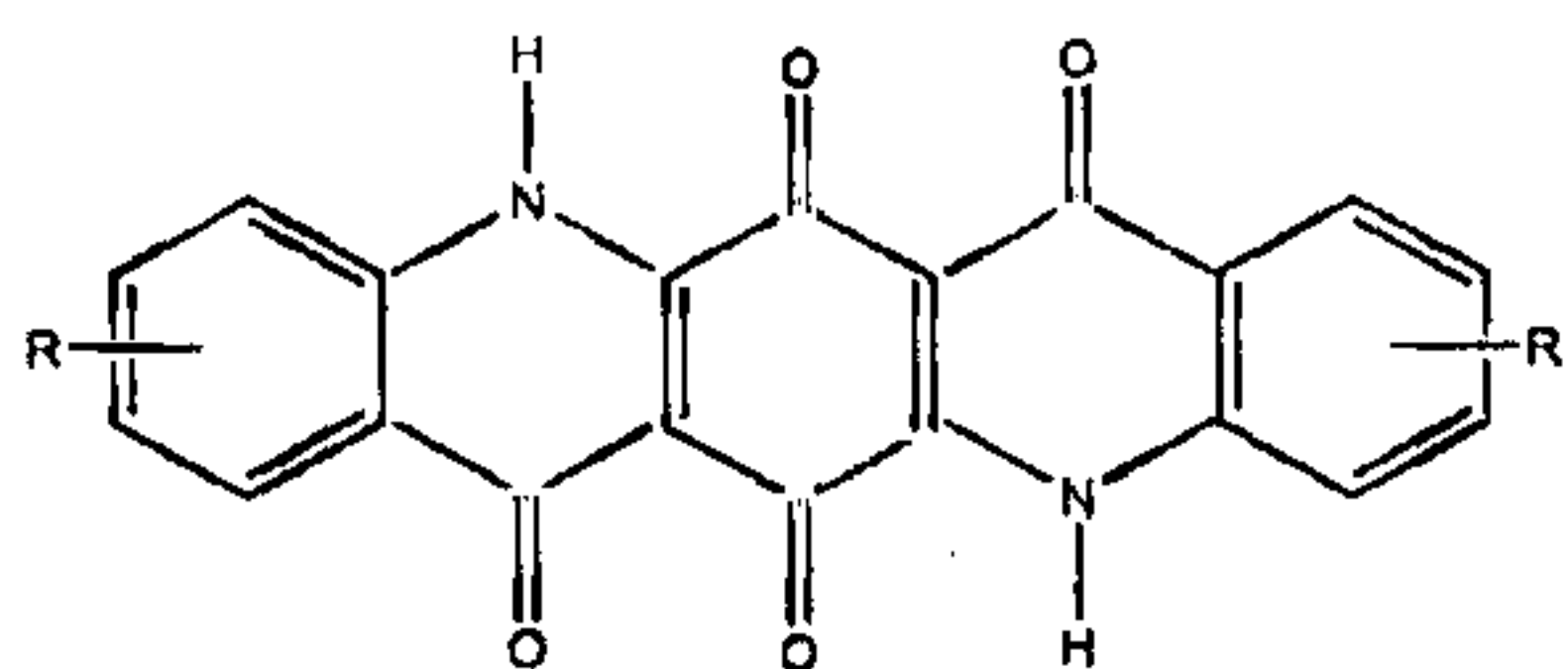
20 [0025] A quinacridone in a liquid medium was prepared by heating polyphosphoric acid (117%;800 grams) to 115°C and adding dianilino-terephthalic acid (200 grams) over a period of three hours at 115-120°C, then maintained at this temperature for 1 hour, and later cooled down to 100°C. Water (15 grams) was added slowly over ten minutes with the temperature maintained at 100-105°C and then further cooled to 80°C. To the  
25 quinacridone in liquid medium was added sodium peroxydisulfate (100 grams) over a four-hour period, the mixture was stirred at 80° C for two hours and then added into water (1 liter). After three hours stirring, the slurry was filtered, the presscake washed-with water to pH 6.5-7.5 and dried, producing a solid solution of 189 grams containing bright yellow highly pure quinacridone and quinacridonequinone.

30 [0026] The invention has been described in terms of preferred embodiments thereof, but is more broadly applicable as will be understood by those skilled in the art. The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention and are intended to be included within the scope of the claims.

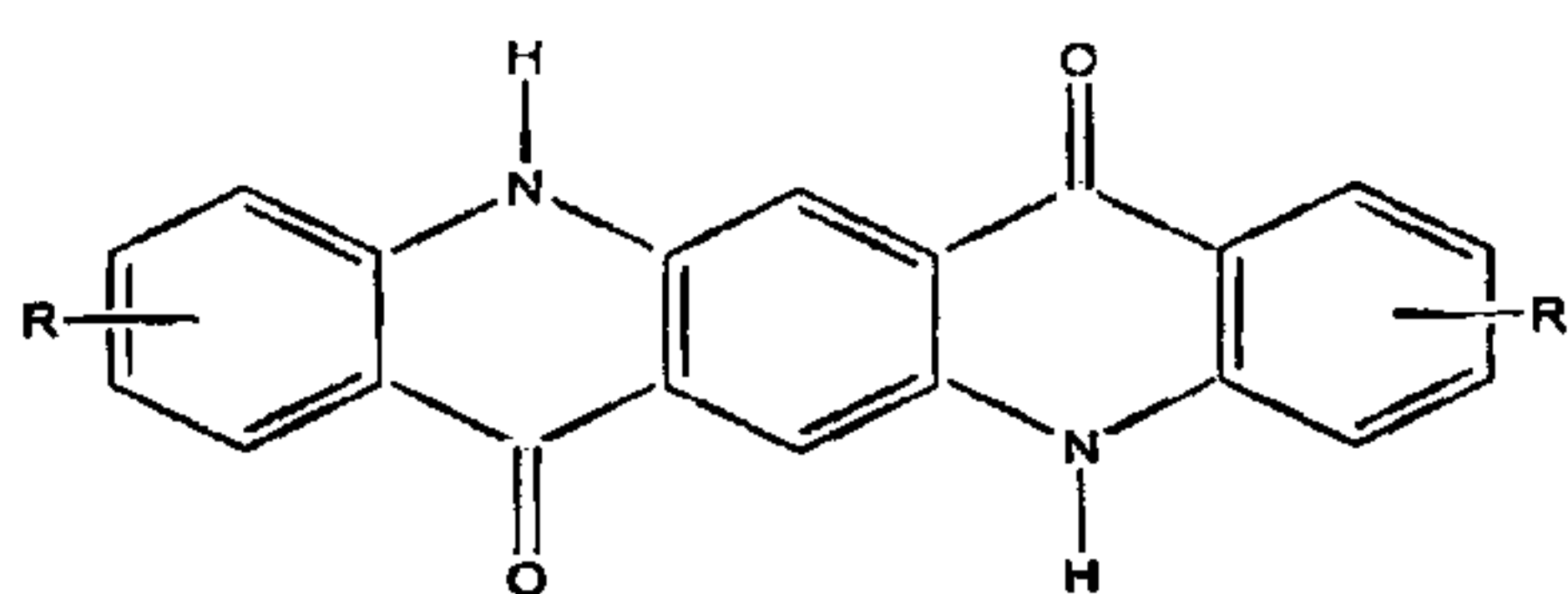
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**CLAIMS**

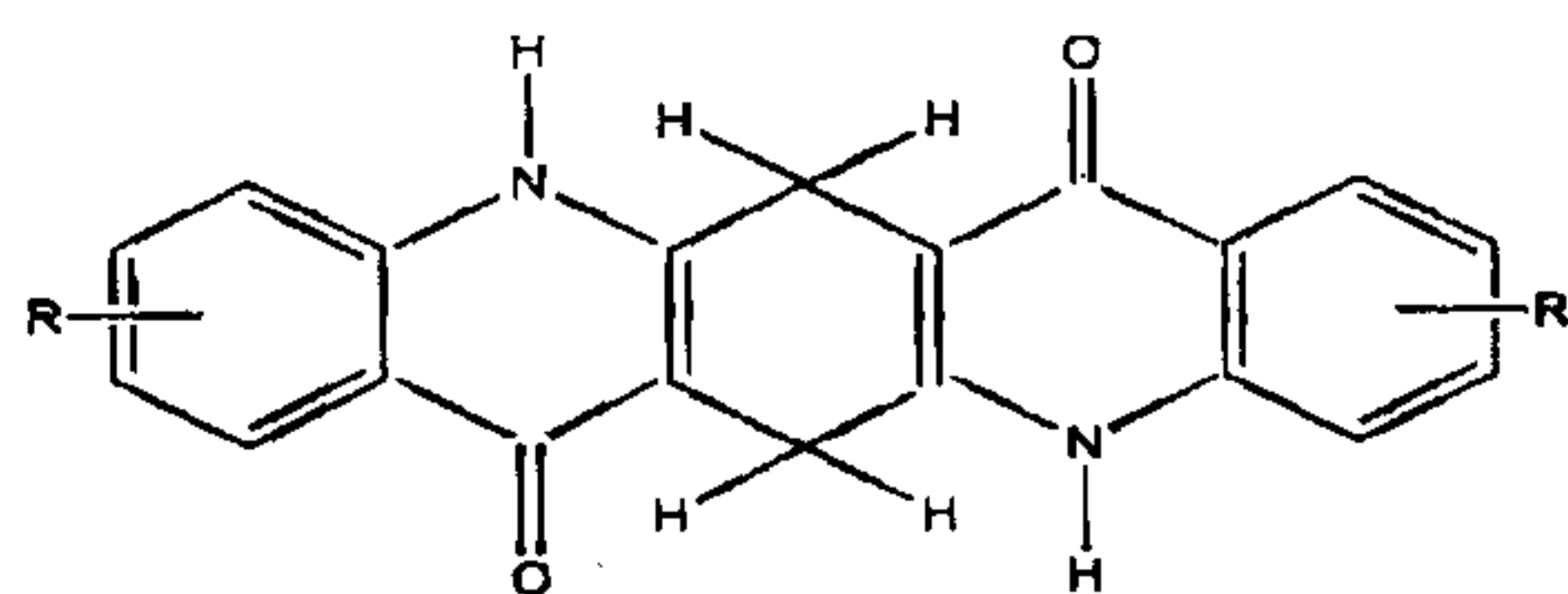
1. A process for preparing a quinacridonequinone of the formula



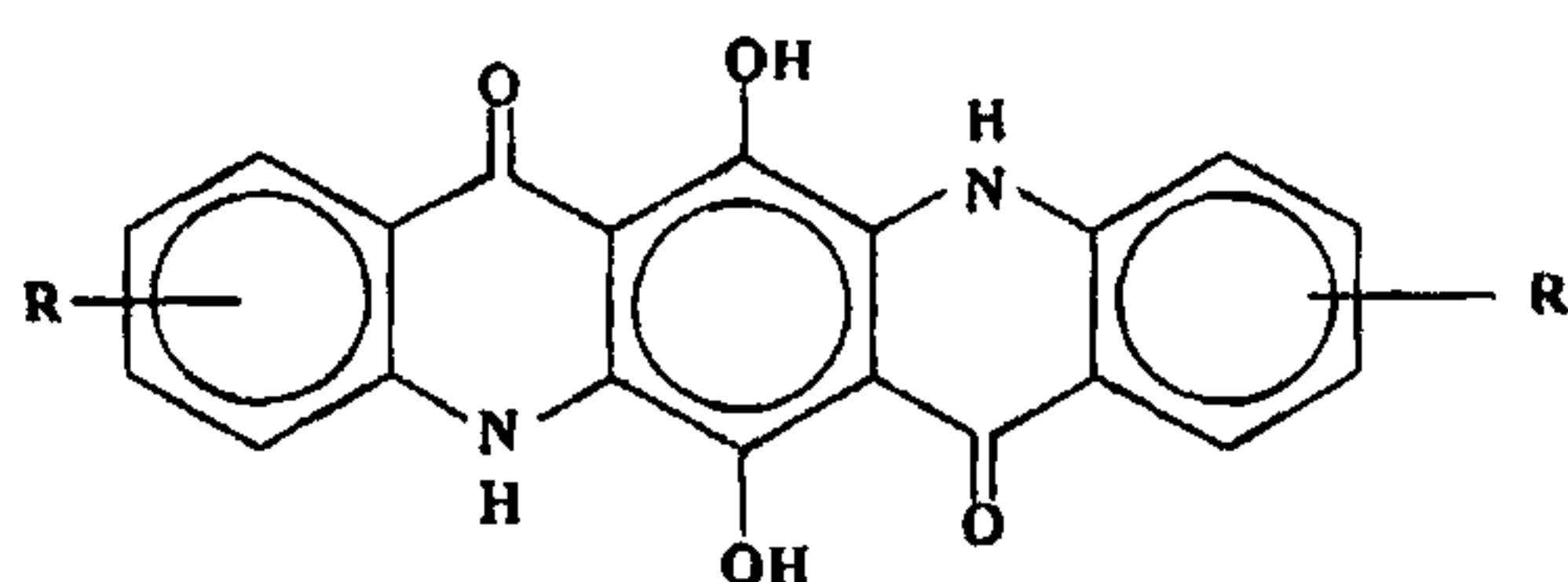
wherein R is selected from hydrogen, halogen, a C<sub>1</sub>-C<sub>10</sub>-alkoxy, a C<sub>1</sub>-C<sub>10</sub>-alkyl, a substituted phenyl, and an unsubstituted phenyl, comprising oxidizing, in the presence of a liquid medium and a non-metal oxidant, a quinacridone of the formula



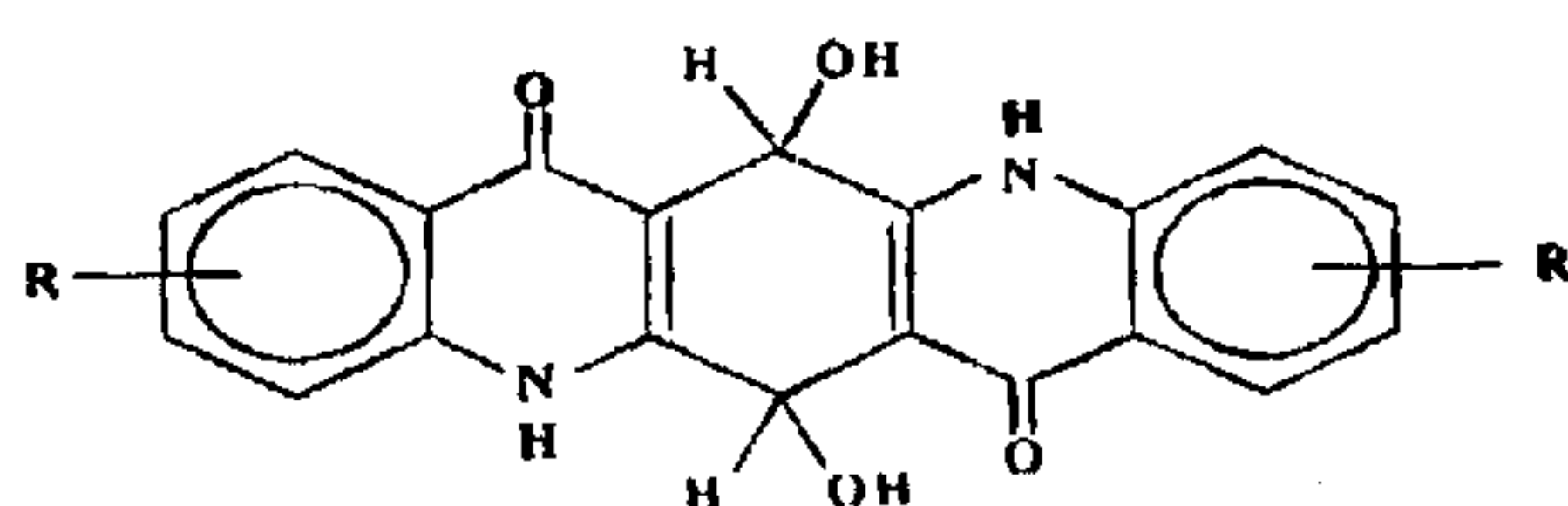
or



or



OR



wherein said non-metal oxidant is selected from persulfuric acid, persulfuric acid salts,

persulfuric acid derivatives, and combinations thereof.

2. The process of claim 1, wherein R is a methyl group.
3. The process of claim 1, wherein R is a methoxy group.
4. The process of claim 1, wherein R is hydrogen.
5. The process of claim 1, wherein R is chlorine.
6. The process of claim 1, wherein said liquid medium is selected from water, an organic solvent, sulfuric acid, polyphosphoric acid, phosphoric acid, acetic acid, and combinations thereof.
7. The process of claim 6, wherein said liquid medium is water.
8. The process of claim 6, wherein said liquid medium is sulfuric acid.
9. The process of claim 1, wherein said non-metal oxidant is a persulfuric acid derivative.
10. The process of claim 1, wherein said non-metal oxidant is persulfuric acid.
11. The process of claim 1, wherein said non-metal oxidant is a persulfuric acid salt.
12. The process of claim 11, wherein said persulfuric acid salt is a peroxydisulfuric acid salt.
13. The process of claim 12, wherein said peroxydisulfuric acid salt is selected from the group consisting of sodium peroxydisulfate, potassium peroxydisulfate, ammonium peroxydisulfate, and combinations thereof.

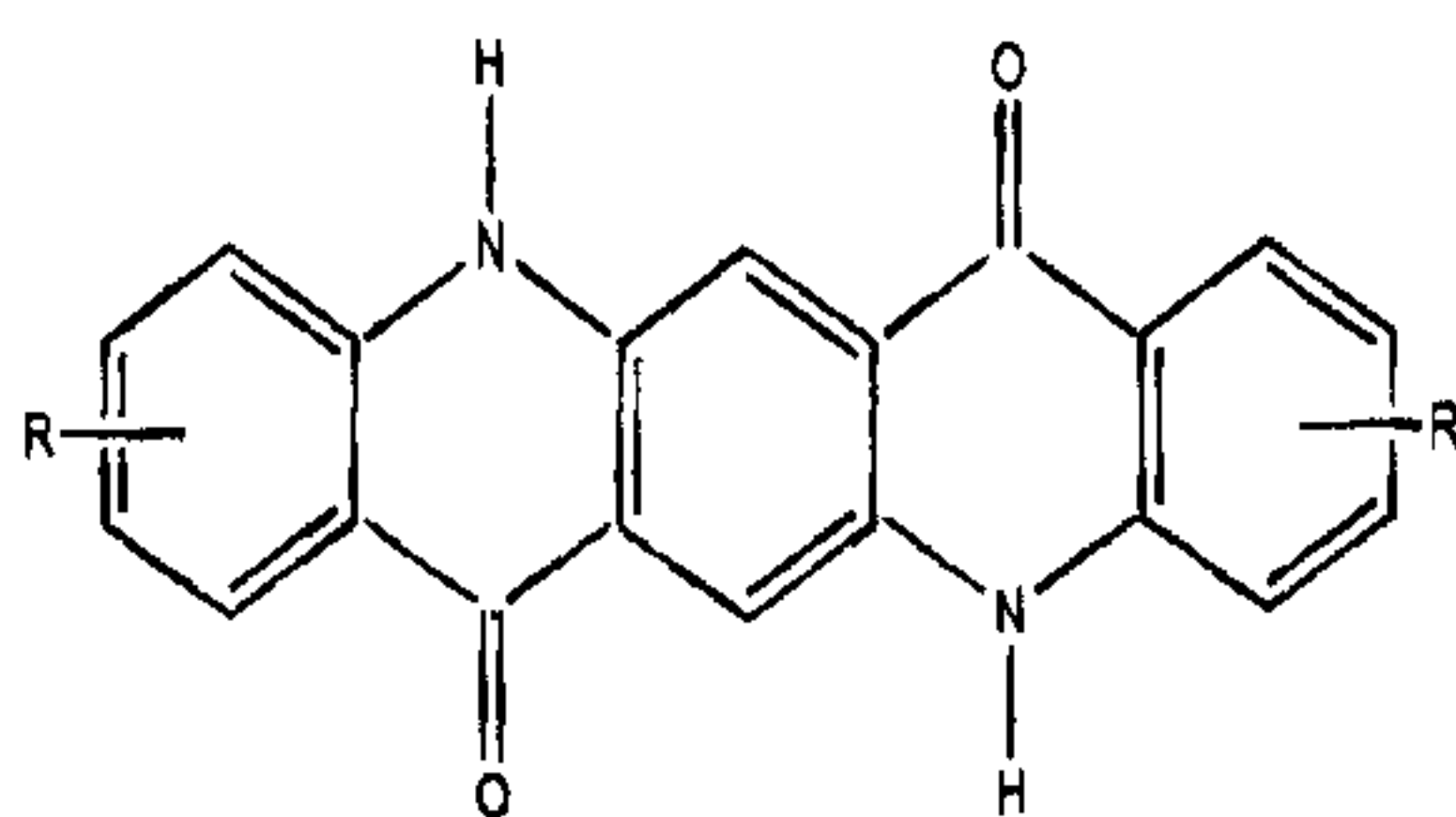
14. The process of claim 13, wherein said peroxydisulfuric acid salt is sodium peroxydisulfate.

15. The process of claim 1, further comprising oxidizing at a temperature ranging from about 28°C to about 85°C.

16. The process of claim 15, wherein the temperature ranges from about 40°C to about 85°C.

17. The process of claim 15, wherein the temperature ranges from about 55°C to about 65°C.

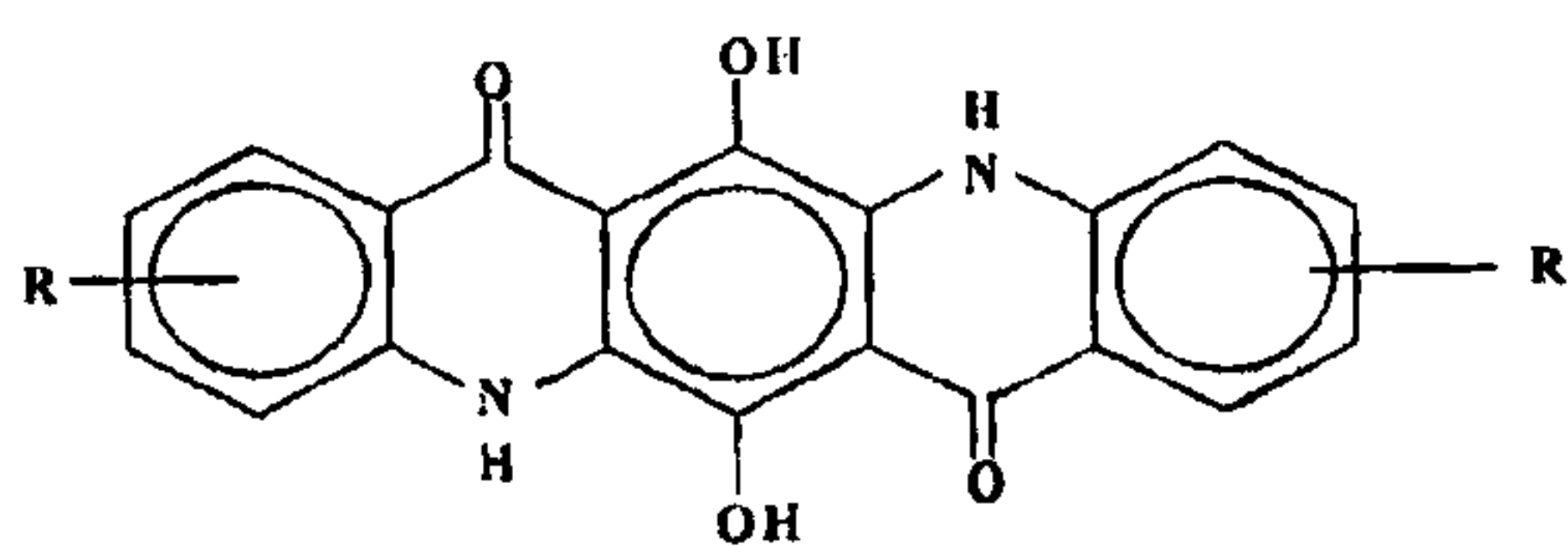
18. The process of claim 1, wherein the quinacridone is of the formula



and is oxidized with sodium peroxydisulfate.

19. The process of claim 18, further comprising oxidizing at a temperature ranging from about 55°C to about 65°C.

20. The process of claim 1, wherein the quinacridone is of the formula

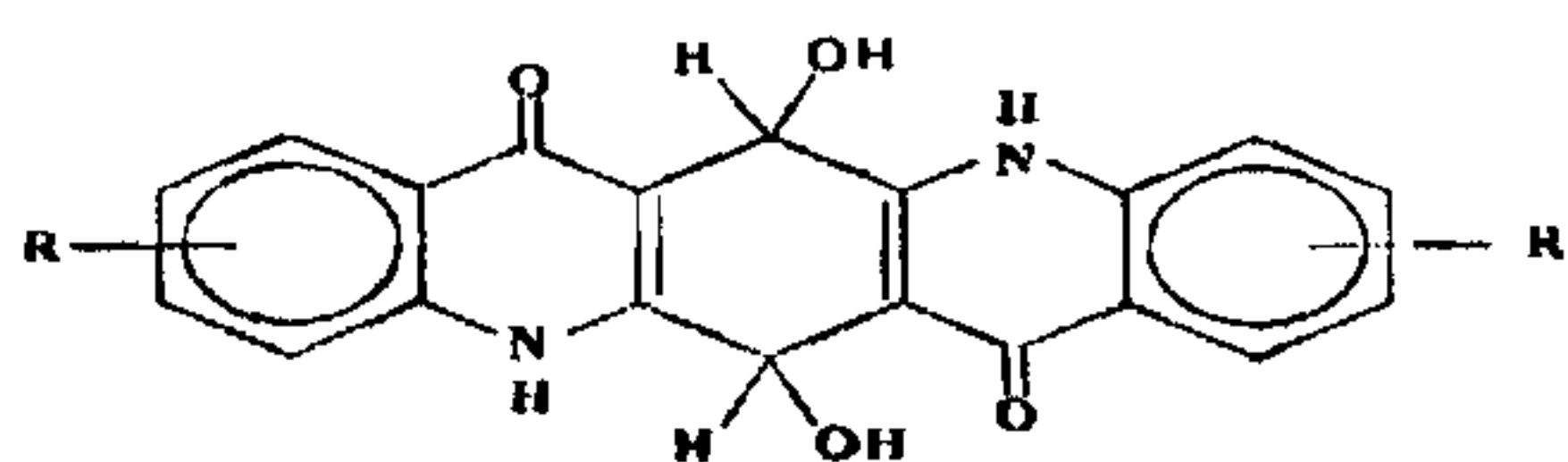


and is oxidized with sodium peroxydisulfate.

21. The process of claim 20, further comprising oxidizing at a temperature ranging

from about 55°C to about 65°C.

22. The process of claim 1, wherein the quinacridone is of the formula

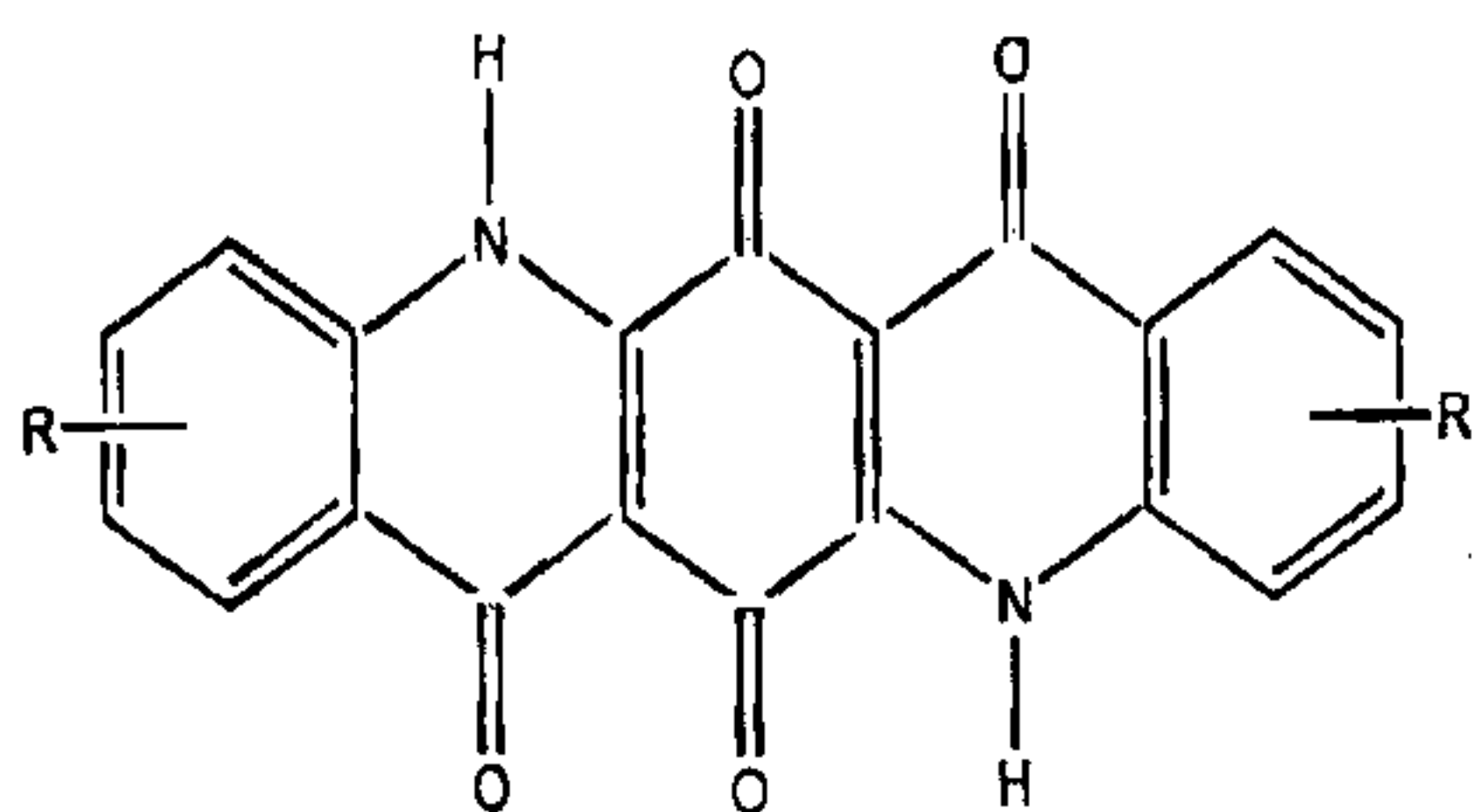


and is oxidized with sodium peroxydisulfate.

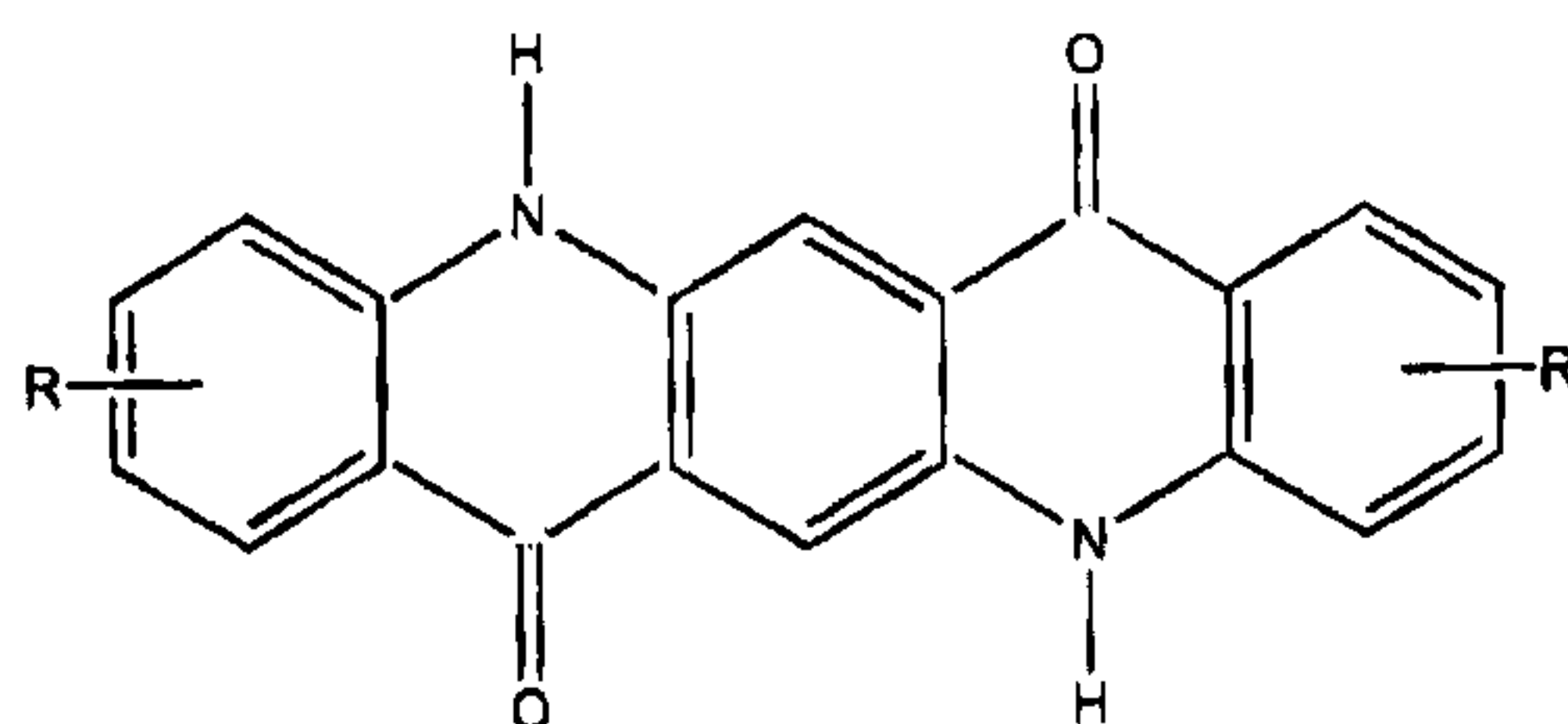
23. The process of claim 22, further comprising oxidizing at a temperature ranging from about 55°C to about 65°C.

24. A quinacridonequinone comprising the product of claim 1.

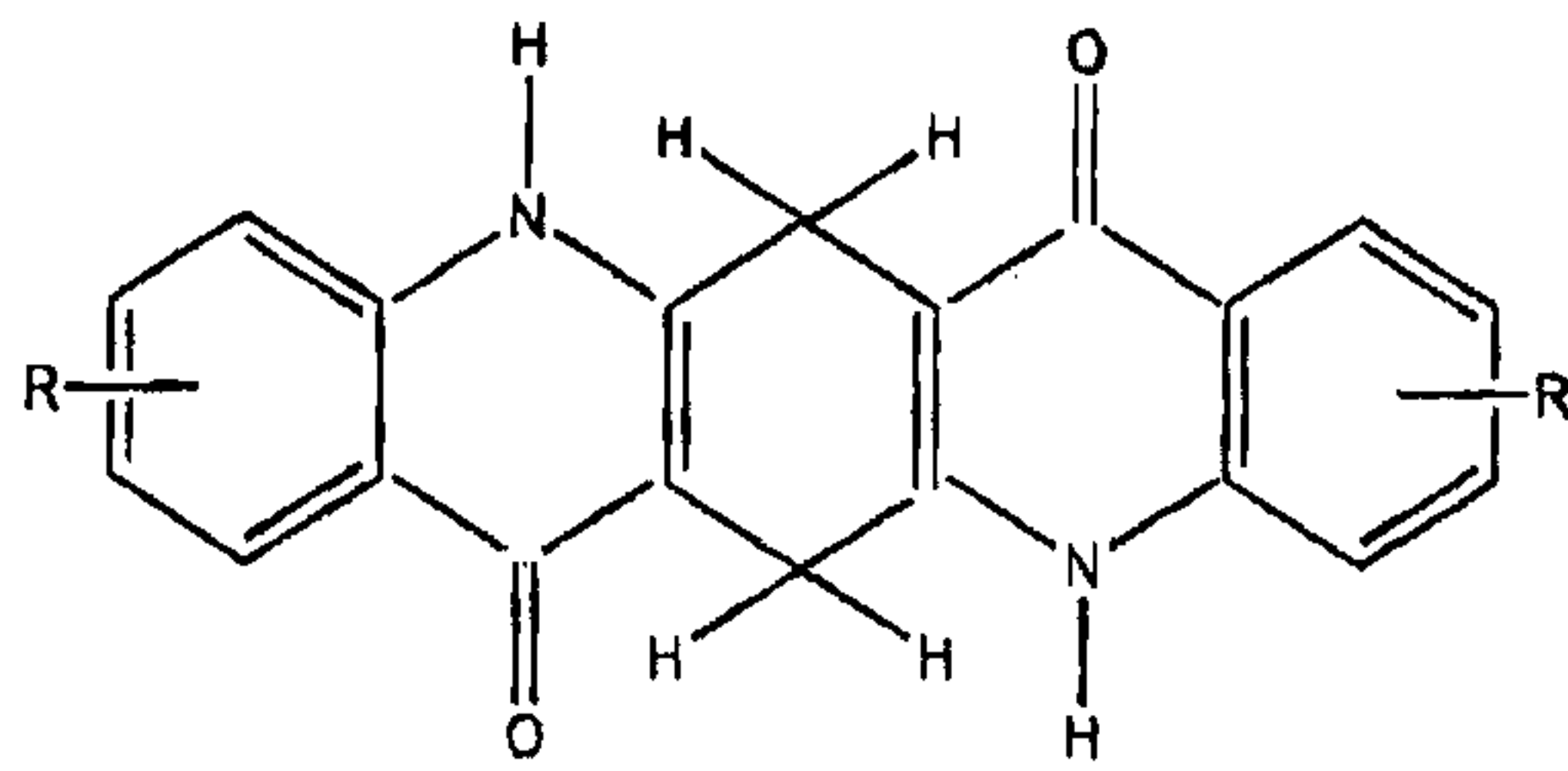
25. A process for improving purity of a quinacridonequinone of the formula



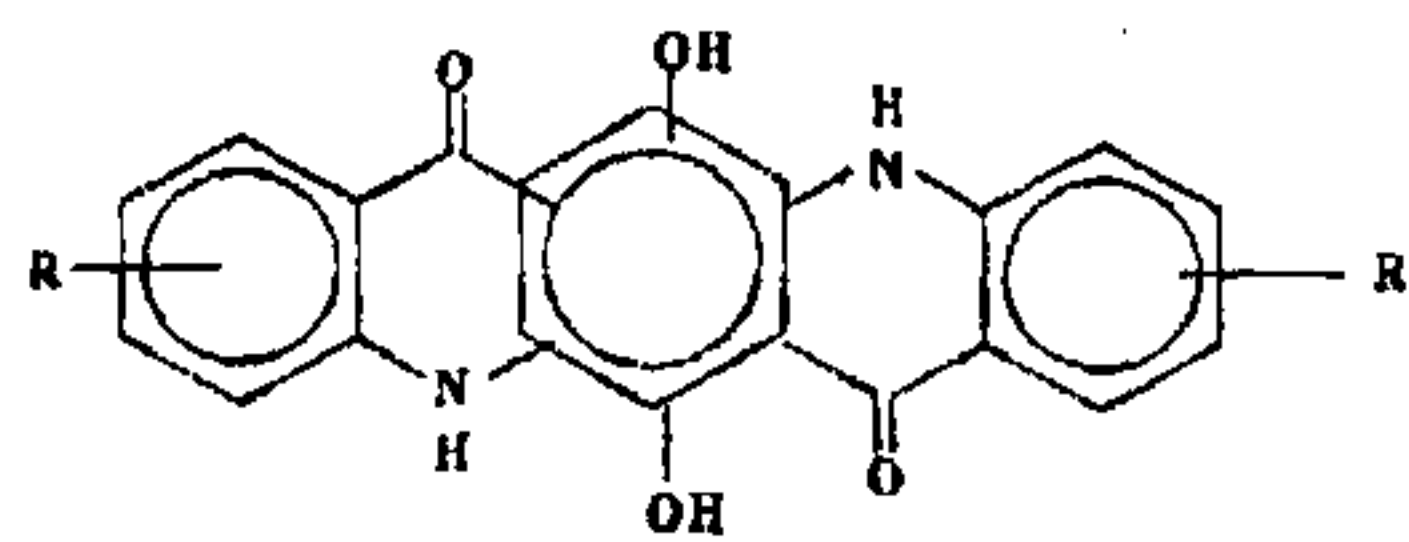
wherein R is selected from hydrogen, halogen, a C<sub>1</sub>-C<sub>10</sub>-alkoxy, a C<sub>1</sub>-C<sub>10</sub>-alkyl, a substituted phenyl, and an unsubstituted phenyl, comprising oxidizing, in the presence of a liquid medium and a non-metal oxidant, a quinacridone of the formula



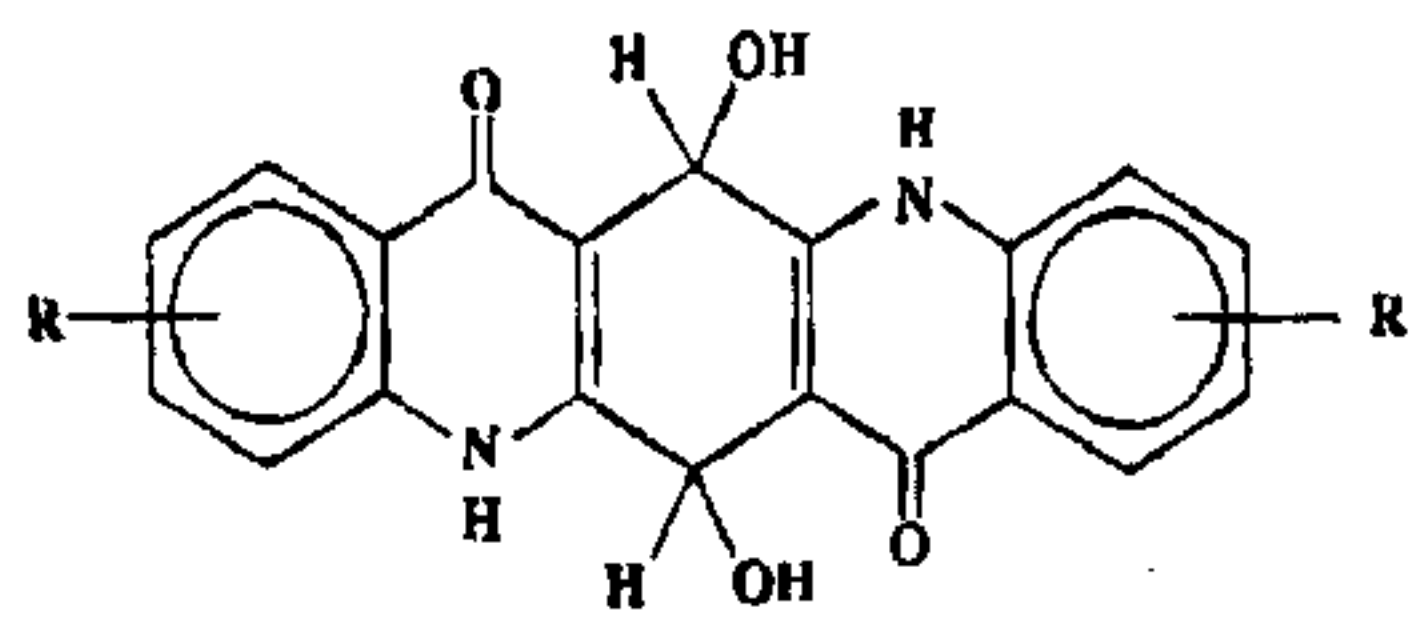
or



or



or



wherein said non-metal oxidant is selected from persulfuric acid, persulfuric acid salts, persulfuric acid derivatives, and combinations thereof.

26. A pigment composition comprising the quinacridonequinone prepared in accordance with the process of claim 1, wherein the quinacridonequinone has a purity ranging from 90% to 98% and is free of metal oxidant.