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2,968,661

1-AMINO-2-BROMO-4-ARYLAMINOANTHRAQUINONE COMPOUNDS

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8 Claims. (Cl. 260—377)

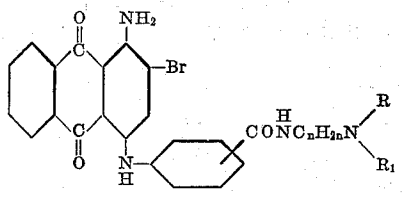
This invention relates to new anthraquinone compounds and their application to the art of dyeing or coloring.

It is well known that polyacrylonitrile fibers are difficult to dye in deep, fast shades without the use of special dyeing techniques, such as, for example, the use of pressure, "carriers" or the so-called "cuprous ion" technique involving the use of acid wool dyes. Each of these methods involves one or more disadvantages. The use of pressure involves the use of pressure equipment which is more expensive than the equipment used where no pressure is involved. The use of "carriers" involves the expense of providing the "carriers." Also, when "carriers" are employed operations for the recovery of the "carrier" for reuse are involved and these recovery operations add to the expense of the dyeing operation.

While many variations in the "cuprous ion" technique have been proposed all suffer some disadvantage. One of the chief disadvantages of this method is the fact that it is almost impossible to restrict the amount of copper absorbed to such a low degree that serious browning of the dyed fabric upon exposure to light does not occur.

It is an object of our invention to provide dyes which can be readily applied to the polyacrylonitrile fibers, especially modified polyacrylonitrile fibers, from ordinary dyebaths. That is, the dyes in finely divided condition are intimately dispersed in water and applied directly to the fiber. Another object of our invention is to provide dyes which yield dyeings on polyacrylonitrile textile materials which have excellent fastness to light and washing. A further object of our invention is to provide dies which are capable of dyeing polyacrylonitrile textile materials in deep shades.

The new anthraquinone compounds of our invention by means of which the objects of our invention can be accomplished have the formula:

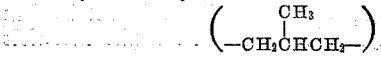


wherein R and R_1 each represent an alkyl group having 1 to 4 carbon atoms, a hydroxy alkyl group having 1 to 4 carbon atoms, a β-methoxyethyl group or a β-ethoxyethyl group, n represents 2, 3 or 4 and wherein



taken together also represent a morpholinyl group or a piperidyl group.

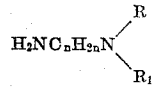
Ethylene, trimethylene, propylene, tetramethylene and 2-methyl trimethylene:



for example, are illustrative of the alkylene radicals represented by C_nH_{2n}.

The new anthraquinone compounds of our invention readily dye polyacrylonitrile textile materials and yield blue dyeings thereon which have excellent fastness to light and washing. They are conveniently applied directly to the polyacrylonitrile textile material from an aqueous dispersion. Deep blue shades can be obtained on polyacrylonitrile textile materials with the new anthraquinone compounds of the invention. Verel and Orlon are illustrative of the polyacrylonitrile materials that can be dyed.

While the anthraquinone compounds of our invention can be prepared by more than one method we prefer to prepare them by condensing the acid chloride of the appropriate 1-amino-2-bromo-4-carboxyanilinoanthraquinone with a primary amine having the formula:



I

wherein n, R, R_1 and

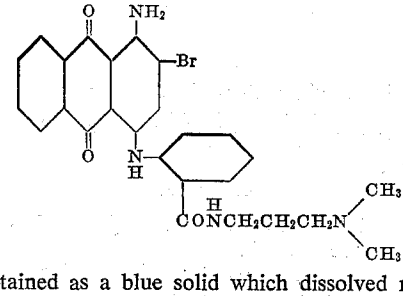


have the meaning previously assigned to them. The acid chloride of the 1-amino-2-bromo-4-carboxyanilinoanthraquinone compound is prepared by known methods.

The following examples illustrate the compounds of our invention and their manner of preparation.

Example 1

One gram of 1-amino-2-bromo-4-o-carboxyanilinoanthraquinone was suspended in 20 cc. of dry chlorobenzene. Two cc. of thionyl chloride were added and the reaction mixture obtained was heated on a steam bath, with stirring, until a clear solution was obtained and no further color change toward the red occurred. The solution thus obtained was cooled to 80° C., diluted with an equal volume of n-hexane and cooled to 20° C. The acid chloride thus prepared was recovered by filtration, washed with n-hexane and sucked dry. The acid chloride product thus obtained was added to 3.5 grams of 3-dimethylaminopropylamine and the resulting mixture was warmed on a steam bath to complete solution. The reaction mixture was then poured into five times its volume of water and the reaction product which precipitated was recovered by filtration and dried at 110° C. 0.95 gram of 1-amino-2-bromo-4-o-[N-(3-dimethylaminopropyl)carboxamido]anilinoanthraquinone having the formula:



was obtained as a blue solid which dissolved readily in warm dilute HCl. It dyes polyacrylonitrile fibers blue shades having excellent fastness to light and wet processing.

Example 2

Ten grams of 1-amino-2-bromo-4-o-carboxyanilinoanthraquinone were suspended in 100 cc. of dry o-dichlorobenzene. 3.4 cc. of thionyl chloride were added and the temperature of the reaction mixture was gradu-

ally raised to 80° C. over a period of about 1.5 hours and held at this temperature for one hour while stirring. Excess thionyl chloride was removed by passing a stream of dry air through the reaction mixture at 65°–70° C. After cooling the reaction mixture to room temperature 2.8 grams of 3-dimethylaminopropylamine and 2.26 grams of anhydrous sodium acetate were added and the reaction mixture was stirred at 70° C.–75° C. for one hour. The reaction mixture was cooled and the product which precipitated was recovered by filtration, washed with n-hexane and then with hot water and dried at 110° C. 11.3 grams of product identical with that prepared in Example 1 were obtained.

Example 3

Example 1 was repeated using 4 grams of 2-dimethylaminoethylamine in place of 3-dimethylaminopropylamine. 1-amino-2-bromo-4-o-[N-(2-dimethylaminoethyl)carboxamido]anilinoanthraquinone was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

Example 4

Example 1 was repeated using 1 gram of 1-amino-2-bromo-4-m-carboxyanilinoanthraquinone and 3.5 grams of 3-dimethyl-aminopropylamine. 1-amino-2-bromo-4-m-[N-(3-dimethylaminopropyl)carboxamido]anilinoanthraquinone was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

Example 5

Example 1 was repeated using 1 gram of 1-amino-2-bromo-4-p-carboxyanilinoanthraquinone and 3.5 grams of 3-dimethylaminopropylamine. 1-amino-2-bromo-4-p-[N-(3-dimethylaminopropyl)carboxamido]anilinoanthraquinone was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

Example 6

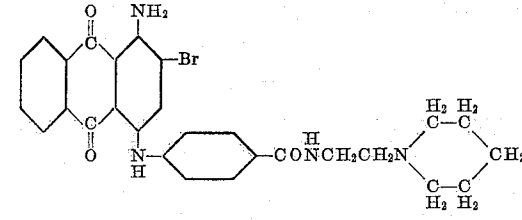
Example 1 was repeated using 4.5 grams of 3-diethylaminopropylamine in place of 3-dimethylaminopropylamine. 1-amino-2-bromo-4-o-[N-(3-diethylaminopropyl)carboxamido]anilinoanthraquinone was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

Example 7

Example 1 was repeated using 1 gram of 1-amino-2-bromo-4-m-carboxyanilinoanthraquinone and 3 grams of 2-diethylaminoethylamine. 1-amino-2-bromo-4-m-[N-(2-diethylaminoethyl)carboxamido]anilinoanthraquinone was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

Example 8

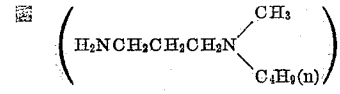
Example 1 was repeated using 1 gram of 1-amino-2-bromo-4-p-carboxyanilinoanthraquinone and 4 grams of N-(2-aminoethyl)piperidine. 1-amino-2-bromo-4-p-[N-(2-piperidylethyl)carboxamido]anilinoanthraquinone having the formula:

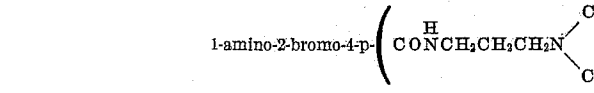


was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

Example 9

Example 1 was repeated using 1 gram of 1-amino-2-bromo-4-p-carboxyanilinoanthraquinone and 5 grams of 3-(N-methyl-N-n-butyl)propylamine



1-amino-2-bromo-4-p-anilinoanthraquinone

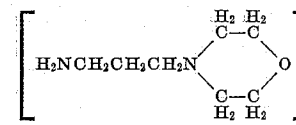
was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

Example 10

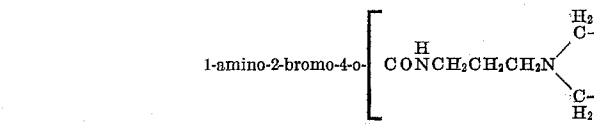
Example 1 was repeated using 6 grams of 3-(di-β-hydroxyethylamino)propylamine in place of 3-dimethylaminopropylamine. 1-amino-2-bromo-4-o-[N-3-di-β-hydroxyethylaminopropyl) carboxamido] anilinoanthraquinone was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

Example 11

Example 2 was repeated using 3.3 grams of 3-(4'-morpholino)propylamine



in place of 3-dimethylaminopropylamine.

1-amino-2-bromo-4-o-anilinoanthraquinone

was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

Example 12

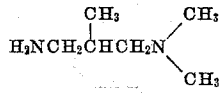
Example 4 was repeated using 4.1 grams of 4-diethylamino-n-butylamine in place of 3-dimethylaminopropylamine. 1-amino-2-bromo-4-m-[N-(4-diethylamino-n-butyl)carboxamido]anilino-anthraquinone was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

By the use of an equivalent amount of 4-dimethylamino-n-butylamine in place of 4-diethylamino-n-butylamine, 1-amino-2-bromo-4-m-[N-(4-dimethylamino-n-butyl)carboxamido]anilinoanthraquinone is obtained as a blue solid. It dyes polyacrylonitrile textile materials

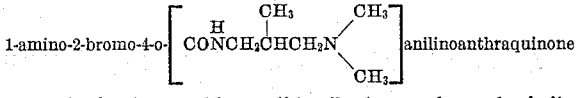
blue shades which have excellent fastness to light and wet processing.

Example 13

Example 2 was repeated using 3 grams of



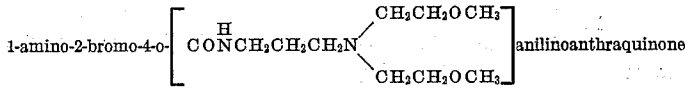
in place of 3-dimethylaminopropylamine.



was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

Example 14

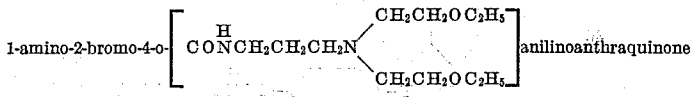
Example 2 was repeated using 3.4 grams of 3-(di-β-methoxyethylamino)propylamine in place of 3-dimethylaminopropylamine.



was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

Example 15

Example 2 was repeated using 4.6 grams of 3-(di-β-ethoxyethylamino)propylamine in place of 3-dimethylaminopropylamine.



was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

Other primary amines that can be used to prepare compounds of our invention include, for example

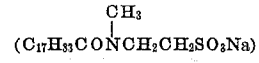
2-di-n-propylaminoethylamine,
2-diisopropylaminoethylamine,
2-di-n-butylaminoethylamine,
2-(di-β-hydroxyethylamino)ethylamine,
2-(di-β-ethoxyethylamino)ethylamine,
3-(di-β-hydroxypropylamino)propylamine,
3-(di-δ-hydroxybutylamino)propylamine,
4-(di-β-hydroxyethylamino)butylamine and
4-(4'-morpholino)propylamine.

The new anthraquinone compounds of our invention can be applied to polyacrylonitrile textile materials from an aqueous dyebath in the same manner that water-insoluble cellulose acetate dyestuffs are commonly applied to cellulose acetate textile materials. Thus they may be directly applied to the polyacrylonitrile textile material undergoing coloration in the form of an aqueous suspension which can be prepared by grinding them to a paste in the presence of a sulfonated oil, soap, sodium lignin sulfonate, or other suitable dispersing agent and dispersing the resulting paste in water. As previously indicated the dyes should be in finely divided condition.

The following example illustrates how the anthraquinone compounds of our invention can be applied to polyacrylonitrile textile materials. As noted hereinbefore the anthraquinone compounds are particularly useful in connection with the dyeing of modified polyacrylonitrile textile materials, such as Verel.

Example 16

16.7 milligrams of the dye compound prepared in Example 1 was dissolved by warming in 5 ccs. of ethylene glycol monomethyl ether. 20 ccs. of a 1% aqueous solution of Igepon T



were added and the volume brought to 200 ccs. by the addition of water at 50° C. Five ccs. of a 30% aqueous solution of formic acid were added, followed by 5 grams of Verel fabric. The temperature was brought to the boil and held there for 1 hour. The cloth was then rinsed in hot water and allowed to dry. It was dyed an attractive blue shade having excellent wash and light fastness. Similar results are obtained when Orlon 42 fabric is used instead of Verel fabric.

The primary amine compounds having the Formula I used in preparing the new anthraquinone compounds of the invention appear to include new as well as old compounds. Many of these amines are specifically disclosed in the prior art. Those not specifically disclosed can be prepared by the methods used to prepare the known compounds. The preferred amine 3-dimethylaminopropylamine is an article of commerce.

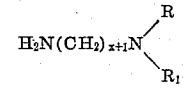
Three general processes by which primary amines having the formula I can be prepared are set forth hereinafter:

(1) an amine having the formula:

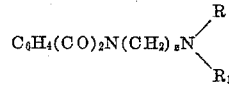


II

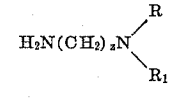
is condensed with a chloroalkylnitrile having the formula: $Cl(CH_2)_xCN$, and the product obtained is reduced by sodium-alcohol or with hydrogen over Raney nickel to give the desired product:



(2) Potassium phthalimide is condensed with a dibromoalkyl compound having the formula: $Br(CH_2)_zBr$ to obtain $C_6H_4(CO)_2N(CH_2)_zBr$ which is treated with II to give



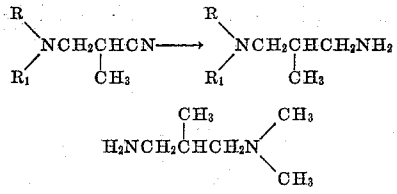
which is hydrolyzed with dilute mineral acid to give



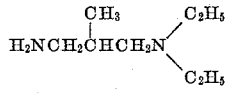
the desired product. Method 2 is the well-known Gabriel synthesis.

(3) A secondary amine is added to an unsaturated

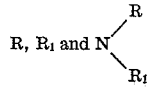
nitrile, e.g. methacrylonitrile, and the product hydrogenated to the primary amine:



and



for example, can be readily prepared by method 3 by reacting dimethylamine and diethylamine, respectively, with methacrylonitrile and then hydrogenating the products obtained to their primary amine form.

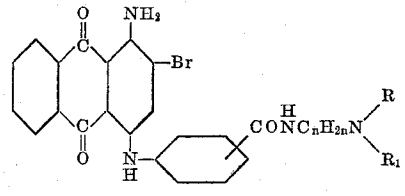


as used herein have the meaning previously assigned to them, while x is 1, 2 or 3 and z is 2, 3 or 4.

The 1-amino-2-bromo-4-carboxyanilinoanthraquinone compounds used in the preparation of the new anthraquinone compounds of our invention can be prepared by the procedure described in Berichte, vol. 49, page 2167 (1916) wherein the preparation of 1-amino-2-bromo-4-o-carboxyanilinoanthraquinone is described.

We claim:

1. The anthraquinone compounds having the formula:



wherein R and R_1 each represents a member selected from the group consisting of an alkyl group having 1 to 4 carbon atoms, a hydroxyalkyl group having 1 to 4 carbon atoms, a β-methoxyethyl group and a β-ethoxyethyl group, n represents a whole number selected from 2, 3 and 4 and wherein

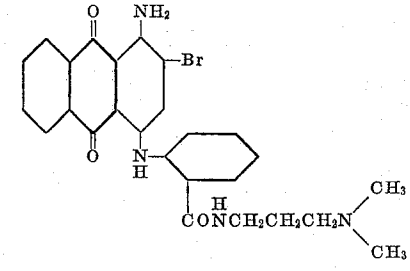


taken together also represent a member selected from the group consisting of a morpholinyl group and a piperidyl group.

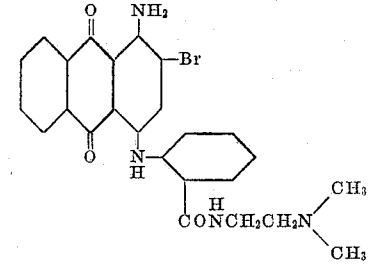
2. The anthraquinone compounds of claim 1 wherein R and R_1 each represents an alkyl group having 1 to 4 carbon atoms.

3. The anthraquinone compounds of claim 2 wherein C_nH_{2n} is $—CH_2CH_2CH_2—$.

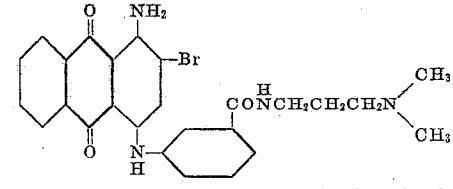
4. The anthraquinone compound having the formula:



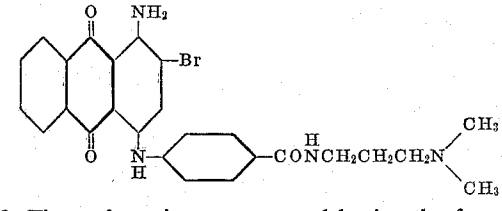
5. The anthraquinone compound having the formula:



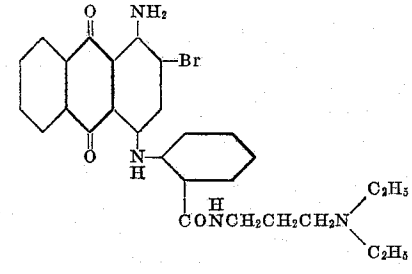
6. The anthraquinone compound having the formula:



7. The anthraquinone compound having the formula:



8. The anthraquinone compound having the formula:



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