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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Quinazoline Pigments

Period Covered September 1969 to December 1970 (Part Time)

KN-71-14

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

TITLE: Quinazoline Pigments

PERIOD COVERED: September 1969 to December 1970 (Part Time)

SUBMITTED BY: J. Auerbach J. Auerbach Date Submitted: 5/3/71

APPROVED BY: E.E.Jaffe E.E. Jaffe Date Released: 6/22/71

ABSTRACT

Several yellow pigments, derivatives of 2-o-hydroxyphenyl-quinazoline, and their non-hydrogen bonded phenyl analogs were synthesized. These internally hydrogen bonded molecules were expected to show greater photostability than their non-hydrogen bonded phenyl analogs and comparable photostability to the photostable parent heterocycle 2-o-hydroxyphenylquinazoline. The hydrogen bonded quinazoline pigments possessed broad visible absorption spectra, which made them tinctorially inferior to the commercial pigments with which they were compared. In terms of lightfastness, the hydrogen bonded quinazoline pigments showed only moderate photostability, a factor which is to date not well understood. In an attempt to circumvent some of the drawbacks of the quinazoline pigments several related hydrogen bonded quinoline pigments were prepared and evaluated. In one case an improvement in color and photostability was observed.

In an area related to the theory of proton transfer in hydrogen bonded molecules several new internally hydrogen bonded quinazoline molecules were synthesized for evaluation as commercial UV absorbers.

TABLE OF CONTENTS

QUINAZOLINE PIGMENTS

PROGRESS REPORT

I. OBJECT

To synthesize yellow organic pigments possessing the o-hydroxyphenylquinazoline moiety. The incorporation of this grouping into pigment molecules was expected to produce compounds with comparable photostability to the photostable parent heterocycle 2-o-hydroxyphenylquinazoline.

II. PERIOD COVERED:

September 1969 to December 1970 (Part Time)

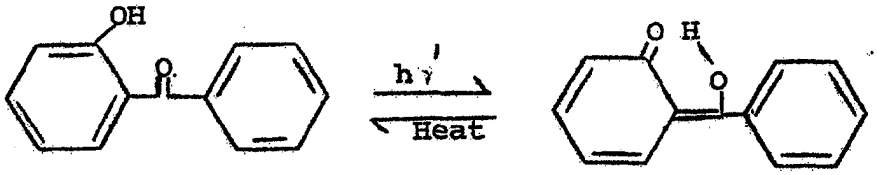
III. PATENT STATUS

The results of this investigation did not warrant the preparation of a patent application

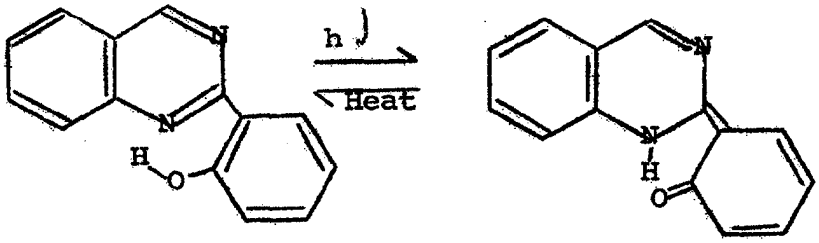
IV. BACKGROUND

It has been known for some time that an improvement in photostability results by attaching a hydroxyl group in the ortho position of benzophenone. There has also been observed an improvement in lightfastness in heterocyclic nitrogen compounds by introducing an o-hydroxyphenyl group so that an intramolecularly hydrogen bonded molecule resulted. The increase in photostability of these molecules is attributed to the following "simplified" energy dissipating photoenolization mechanism:

Benzophenones

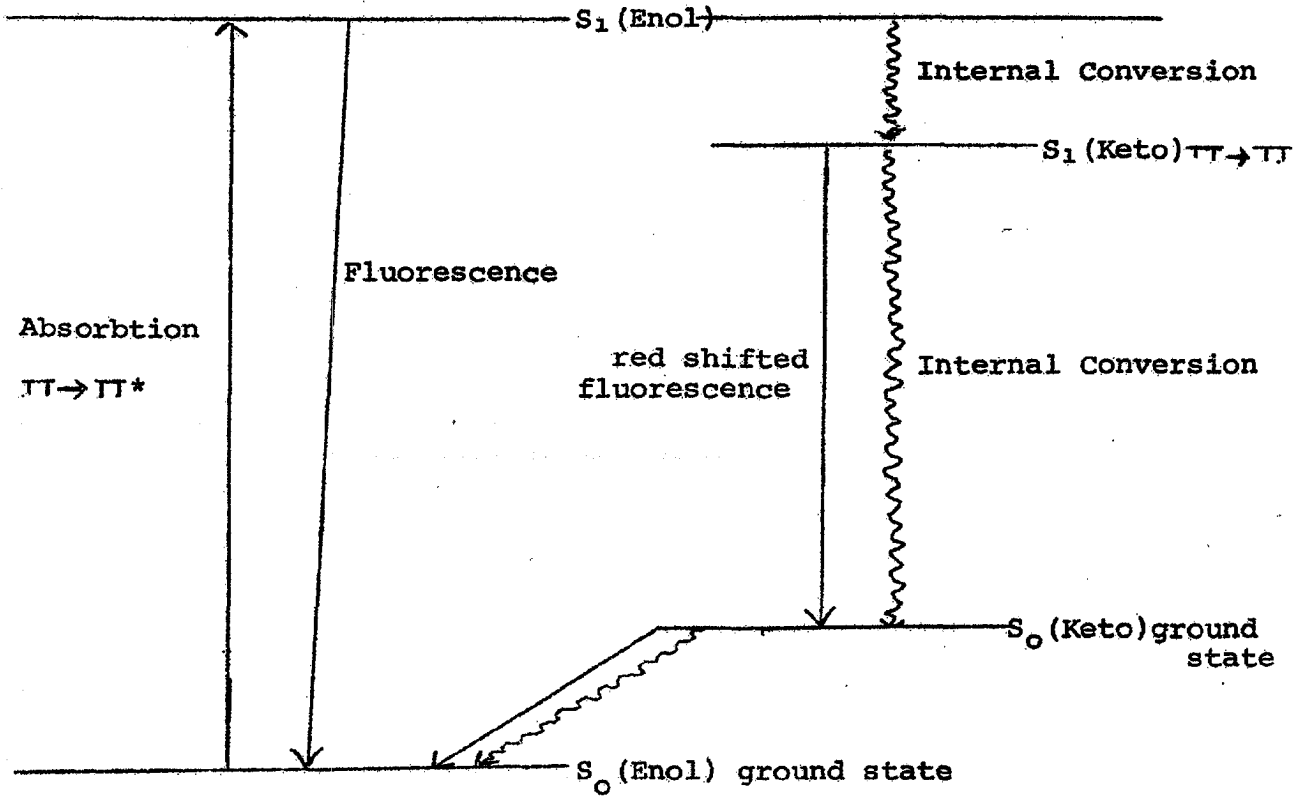


O-hydroxyphenyl-quinazoline



A large measure of understanding of this mechanism of stabilization came from the theoretical work of J.E. Otterstedt. Simply stated, he postulated that light energy absorbed by the ground state (enol) converted it to its first excited singlet state. Proton transfer from this singlet state could then occur to produce the first excited singlet state of the keto isomer, which could then dissipate its energy in the form of heat by ultimately reverting to its enol ground state. To substantiate this theory very weak red

shifted fluorescence has been observed from intramoleculary hydrogen bonded benzophenones, triazolines, pyrimidines, quinolines, and quinazolines. The observed red shifted fluorescence was then correlated with the S_1 (keto) $\rightarrow$ S_o (keto) transition in the emission spectra of these compounds.



The relative stability of o-hydroxyphenyl nitrogen heterocycles has been found to be proportional to the change in resonance energy in going from the S_1 (enol) to S_1 (keto) states. Thus it has been found that the photostability of various o-hydroxyphenyl heterocycles can be put in the following order.

quinazoline > quinoline > triazine > pyrimidine > pyridine

This order is reasonable in view of the increasing resonance stabilization of the molecules shown above.

Of the various heterocycles tested the 2-(o-hydroxyphenyl)quinazoline system possessed the highest photostability. This finding formed the basis of the attempt to synthesize pigment molecules possessing this photostabilizing heterocyclic moiety.

The theory as advanced by Otterstedt, has found practical application in the synthesis of quinazoline UV absorbers. Ideally UV absorbers are colorless materials which absorb strongly in the UV but which are themselves photostable.

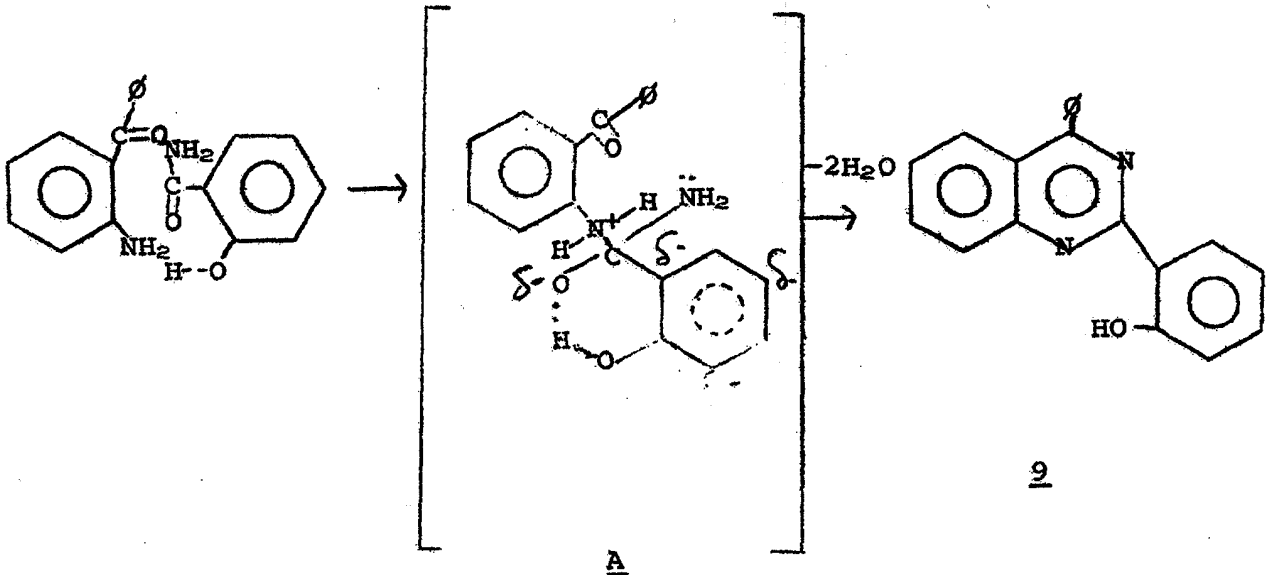
By the technique of over-coating the UV absorber it has been

demonstrated that these compounds could afford significant protection against harmful radiation and protect otherwise insufficiently stable pigments. One drawback to the quinazoline UV absorbers has been their slight yellow coloration. This is due to the tail end of their UV absorption band. It occurred to us that if the yellowness observed in low molecular weight o-hydroxyphenyl-quinazolines could be enhanced through conjugation then this might make the basis for a light stable yellow pigment.

V. SYNTHESIZED COMPOUNDS

There are a number of synthetic routes to the quinazoline nucleus. However, in the course of the work synthetic limitations to their usefulness were encountered. It was discovered quite fortuitously that the reaction between o-hydroxybenzamides and aromatic aminoketones produces the quinazoline nucleus by simple thermal condensation.

Below is a proposed reaction mechanism which accounts for the ready interaction of the amide and amine and rationalizes the fact that unsubstituted benzamide reacts only to produce simple amides. The synthesis of the valuable UV absorber 9 is presented

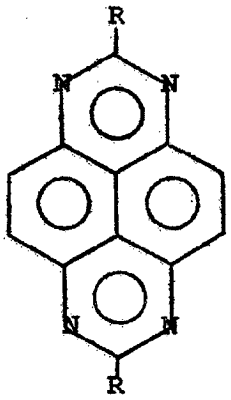


A

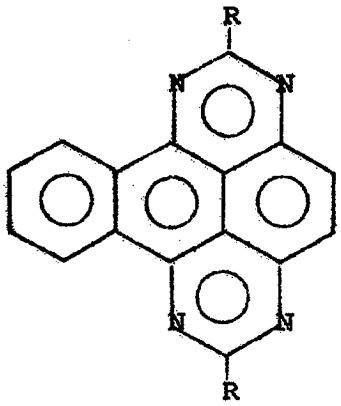
9

The probable long lifetime of intermediate A allows the amide - NH_2 to attack the -C=O of the benzophenone leading to quinazoline ring formation, whereas in simple benzamides such a stabilized intermediate is not possible. In contrast the strong negative charge initially placed on the -C=O of benzamide leads to ejection of ammonia and simple amide formation. For example: the reaction of banzamide with 1,5-diaminoanthraquinone yields 1,5-dibenzoylaminanthraquinone. Under comparable conditions salicylamide yields the heterocycle 3b.

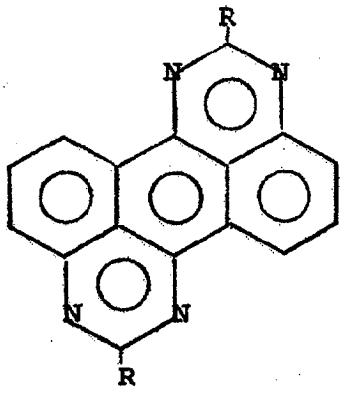
The following yellow quinazoline pigments have been prepared. Their structures are assigned on the basis of elemental analysis, IR, and UV spectroscopy. Additional evidence is presented where alternative synthetic routes were successful to substantiate the proposed structure.



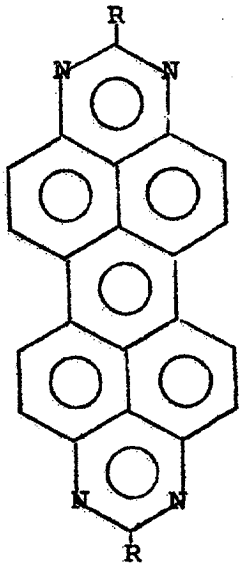
1 a) R=CH_3
b) R=phenyl
c) R=ortho-hydroxyphenyl (OHP)



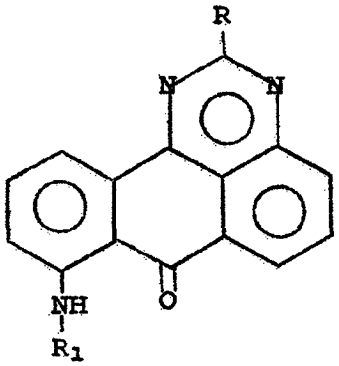
2 R=OHP



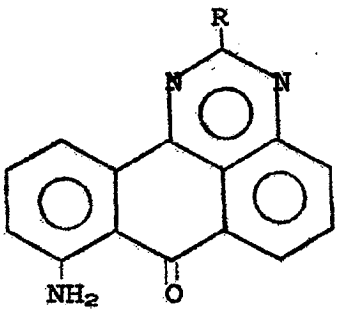
3 a) R=phenyl
b) R=OHP
c) R=2-hydroxy-3,5-dichlorophenyl



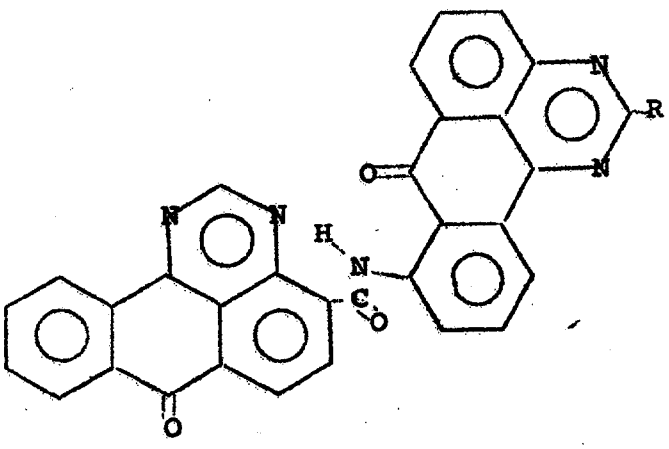
4 a) R=CH_3
b) R=phenyl



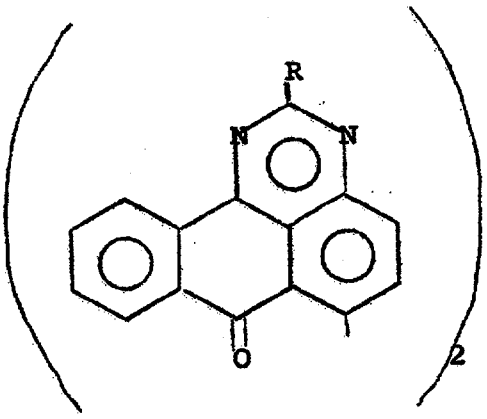
5 R=OHP
R_1=benzoyl



6 R=OHP

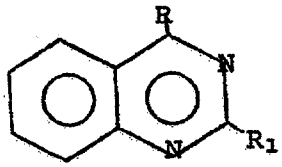


7 R=OHP

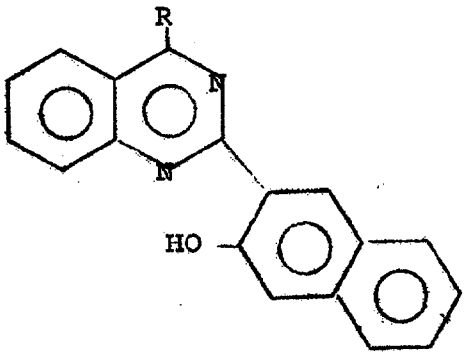


8 a) R=phenyl
b) R=OHP

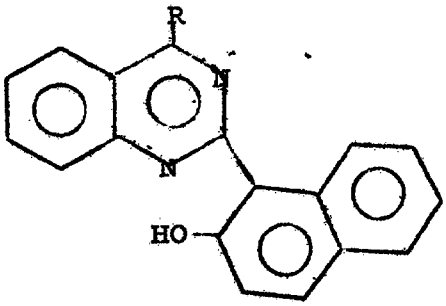
Essentially colorless compounds prepared to be tested as UV absorbers are shown below:



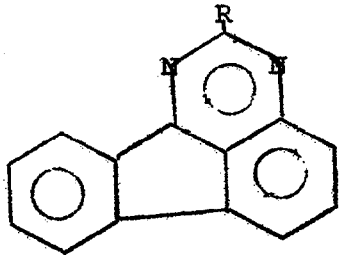
9 R=phenyl
R_1=OHP



10 R=phenyl

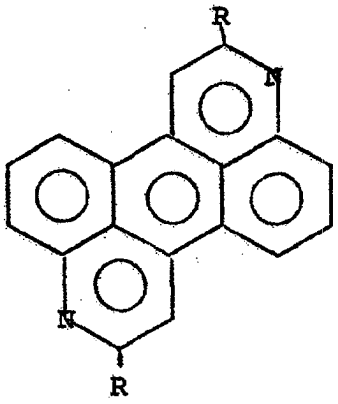


11 R=phenyl

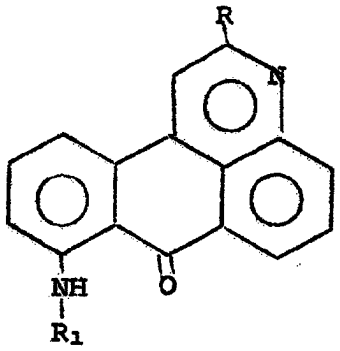


12 R=OHP

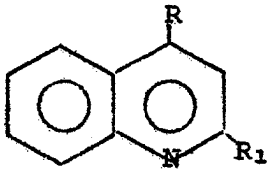
In the course of the work other related compounds were prepared and are presented below:



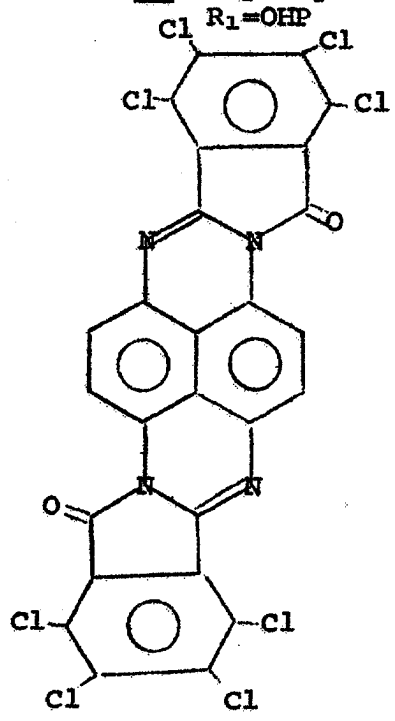
13 R=OHP



14 R=OHP
R_1=benzoyl



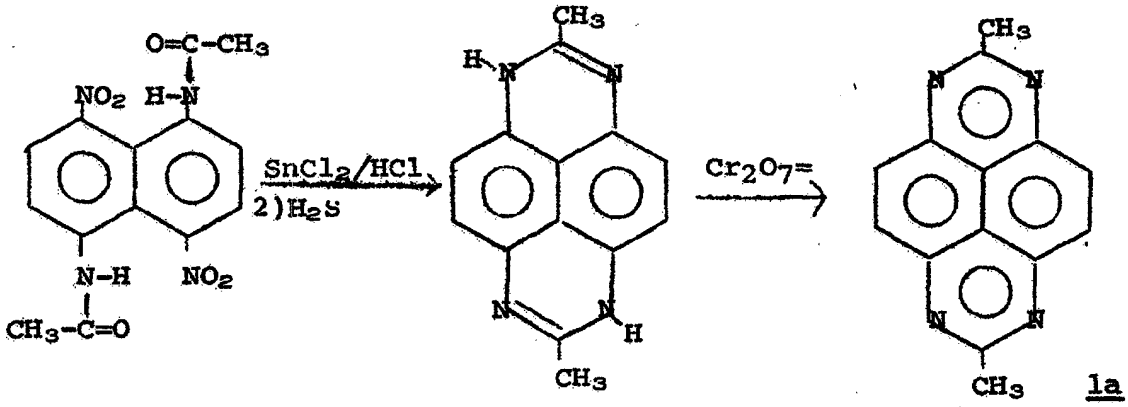
15 R=phenyl
R_1=OHP

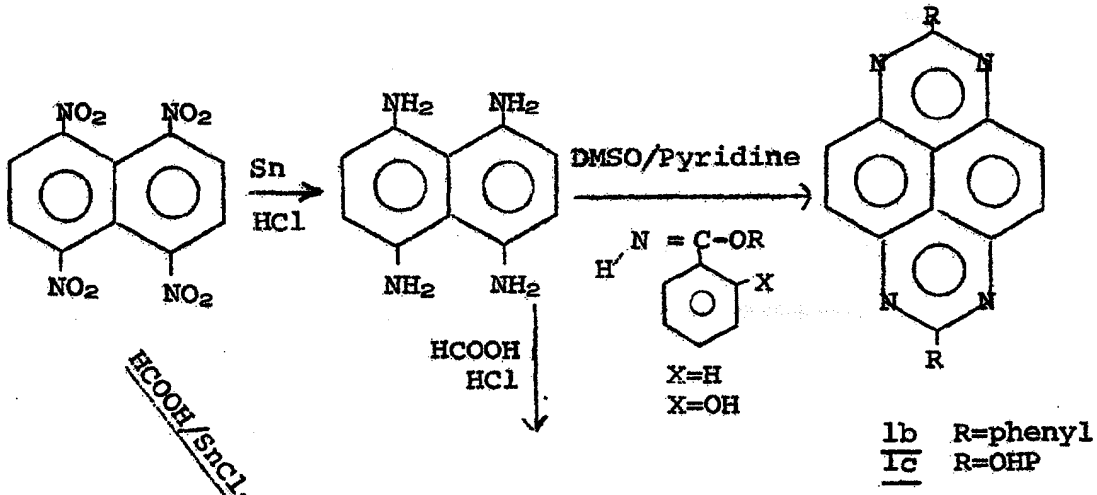


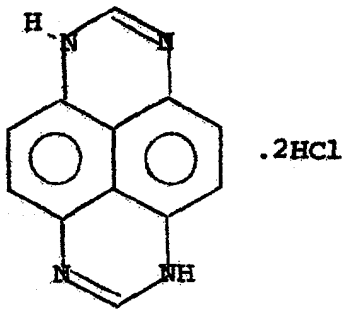
16 cis and trans

Synthesis

A search of the literature revealed that compound 1a and 1b were prepared by Plumpe, Belg. Pat. G59016. They were reported to be yellows. Compound 1b was reported to be in fact a strong yellow.



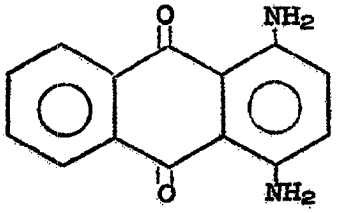




B

The synthesis of 1c depended on the isolation of naphthalenetetramine. However, difficulty was encountered in preparing the material described in the literature. In order to confirm our isolation of this tetramine, it was converted to the known compound B.

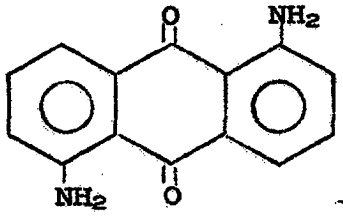
Synthesis of 2



Salicylamide → 2

Synthesis of 3

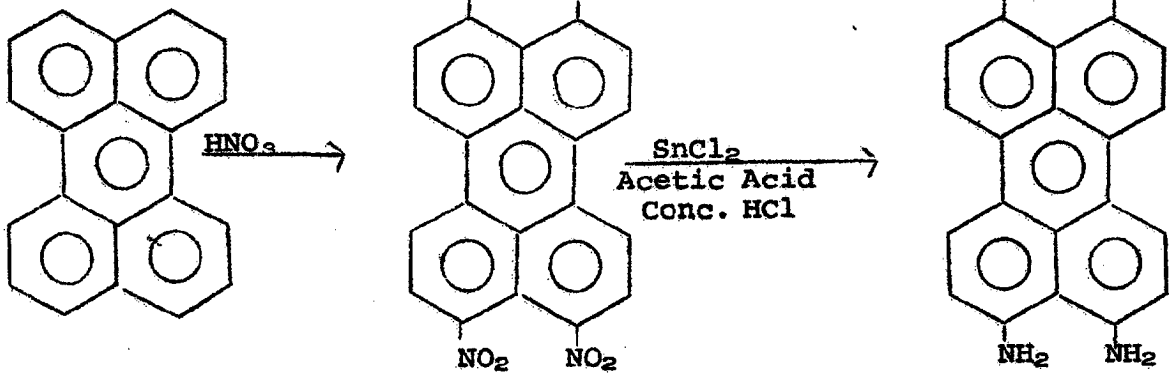
3a ← Benzaldehyde / Ammonia/Nitrobenzene



Salicylamide → 3b

→ 3c (3,5 Dichloro-salicylamide)

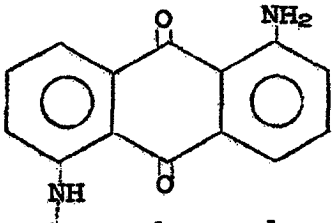
Synthesis of 4



Tetramine —(Acetic Anhydride / Pyridine)→ 4a

Tetramine —(Benzoic Anhydride / Pyridine)→ 4b

Synthesis of 5



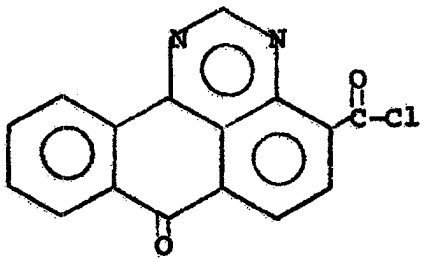
Salicylamide → 5

Synthesis of 6

R=benzoyl

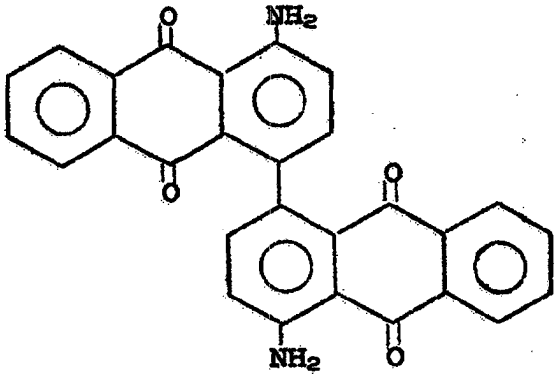
5 —(Dilute H_2SO_4)→ 6

Synthesis of 7



+6 Nitrobenzene, Heat → 7

Synthesis of 8



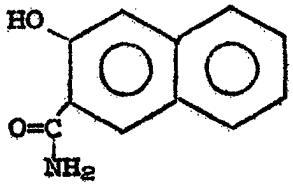
Benzonitrile/H^+ → 8a

Salicylamide/250° → 8b

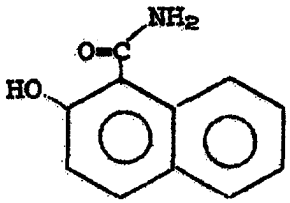
2 Hydroxy-benzonitrile, H^+/Heat → 8b

(Ciba) Chromophthal Red 3B

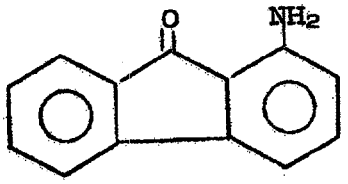
Synthesis of 10

2-aminobenzophenone +  diglyme, reflux → 10

Synthesis of 11

2-aminobenzophenone +  diglyme, reflux → 11

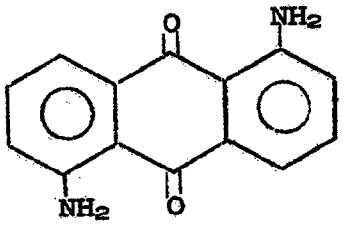
Synthesis of 12



2-hydroxybenzonitrile/H^+ → 12

Salicylamide, Heat → 12

Synthesis of 13



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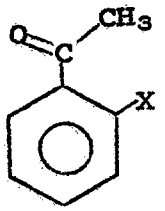
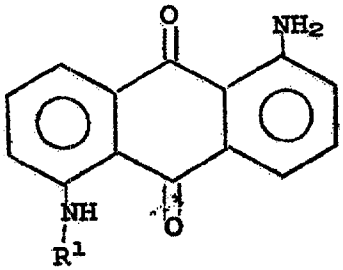


X=OH

Reflux → 13 X=OH

Synthesis of 14



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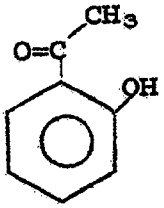
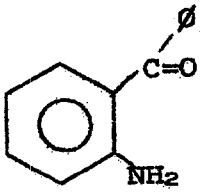


→ 14

Synthesis of 15



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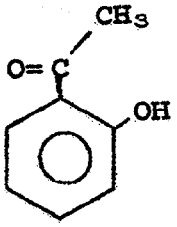
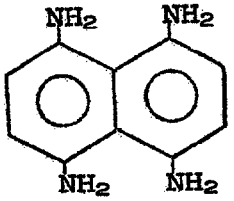
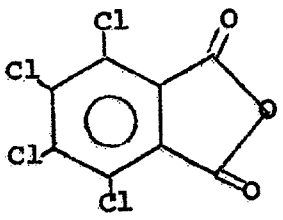


Reflux → 15

Synthesis of 16



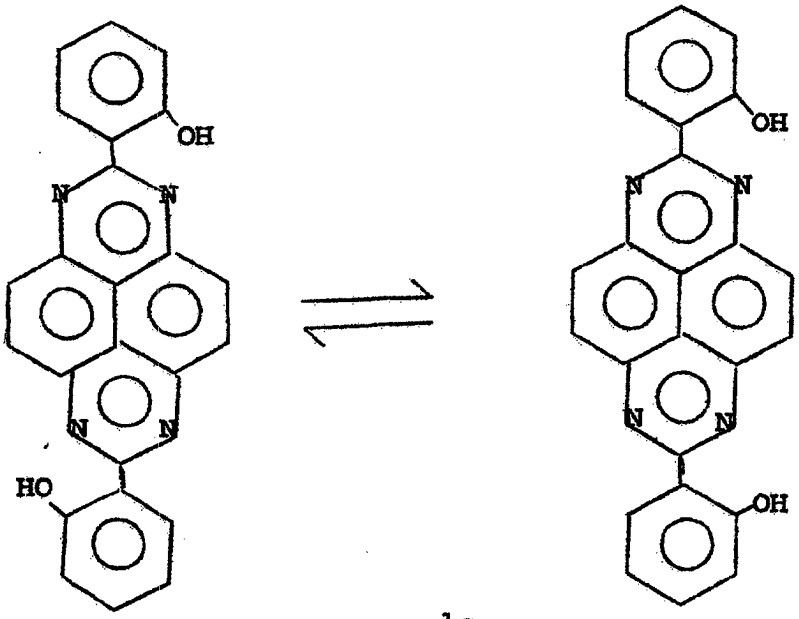


Sodium Acetate, Acetic Acid, Reflux → 16

Discussion

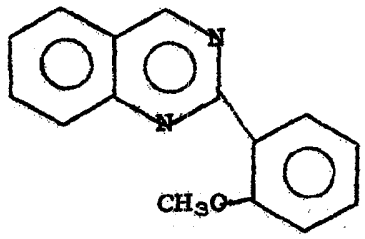
Compounds 1a,b,c were prepared to examine their absorption spectra and photostabilities. Compound 1a shows its highest λ max at 381 nm (ϵ 6,677) and its longest wavelength absorption at 400 nm (ϵ 398), in DMF solution.

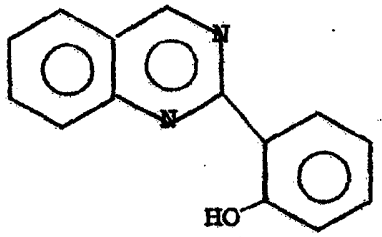
Comparing 1a to the hydrocarbon pyrene is revealing in that the hydrocarbons longest wavelength maximum in DMF solution occurs at 337 nm (ϵ 44,673), while in the spectrum of 1a one does not see any absorption above 300 nm of an extinction coefficient greater then 6,700. Therefore, in comparing 1a to pyrene one sees a marked drop in extinction of 1a relative to pyrene and also a bathochromic shift of the longest wavelength maximum. In DMF solution compound 1b R=phenyl shows a reasonably sharp absorption at λ max 421 nm (ϵ 3,136), whereas compound 1c displays very broad absorption in the visible, its highest absorption occurring at 430 nm (ϵ 2,043). Comparing compound 1b to 1a one sees a shift to longer wavelength due to additional phenyl conjugation but still a reasonably low extinction, of the longest wavelength maximum. It is noteworthy that 1c (R=OHP) shows a broad absorption in the visible spectrum. This broadness has been noticed in the visible absorption spectra of other ortho-hydroxyphenyl quinazoline pigments. Two reasonable explanations might be advanced to explain this phenomenon. Firstly, the introduction of the hydroxyl in the ortho position extends the conjugation of the system by forcing the phenyl moiety to lie in the plane of the tetrazapyrene ring. Secondly, due to the possibility of the existence of two distinct conformational arrangements as a consequence of the two sites of hydrogen bonding available to each (OHP) group, we may be seeing the visable spectra of two different molecules in solution.



1c

That intramolecular hydrogen bonding is very likely present in 1c is deduced from the bathochromic shift of 1c relative to 1b in analogy with the bathochromic shift observed in the spectrum of the hydroxy vs. the methoxy compound shown below.





λMax 316 nm (Methyl pentane) λMax 334 nm (Hexane)

Whether the broadness of absorption in the spectrum of 1c is due to the presence of an equilibrium between rotomers or is inherent in this type of intramolecularly hydrogen bonded molecules cannot be decided unequivocally. This point will, however, be clarified when the spectra of 5 and 14 are compared.

In addition, other evidence which bears on the co-planarity of 1c comes from a comparison of the melting point of 1b (334°C) with that of 1c (430°C). The higher melting point of 1c is consistent with it being hydrogen bonded, and thus completely planar and more symmetrical.

In summary, the introduction of hydrogen bonding in compound 1c results in a broadening of the visible absorption spectrum of this compound relative to the phenyl derivative. The broadness of absorption is an important consideration in that it adversely affects the intensity of color of these types of compounds.

The lightfastness of compound 1b and 1c were evaluated by Fadeometer exposure. Both 1b and 1c were dispersion milled and both tints (1/25) and masstones were compared against Anthrapyrimidine Yellow. After 300 hrs. exposure 1b showed a marked darkening in masstone and fading in tint. Whereas 1c showed only moderate darkening in masstone and a slight darkening in tint. By comparison the standard Anthrapyrimidine Yellow showed only a slight fading both in tint and masstone after 300 hours exposure. These effects were more pronounced when both 1b and 1c were acid pasted and flushed and compared in the usual way by Fadeometer exposure. At this point it was of interest to prepare other quinazolines possessing more intense color and better photostability.

Compound 2 a benz-fused pyrene displayed enhanced longest wavelength absorption relative to 1c. Although the absorption was also broad, it attained its highest value at 445 nm (ϵ 3884) in DMF solution. The broadness of the band is indicated by its absorption at 490 nm (ϵ 1776). A lightfastness determination on 2 was performed with crude material. Tint (1/50) and masstone were prepared and compared against Irgazin 3 RLT. In masstone 2 displayed comparable lightfastness to Irgazin after 225 hours Fadeometer exposure, but

in tint if faded at a rate slightly faster than Irgazin. The main drawbacks of 2 are its dullness and relatively low strength.

The synthesis of compound 3a was accomplished via the route outlined in the literature. The synthesis of 3b has been accomplished via the reaction between salicylamide and 1,5-diaminoanthraquinone as outlined earlier. The synthesis of 3b has been accomplished earlier by P.S.Dhaliwal by reacting 1,5-disalicoylaminoanthraquinone under high pressure with ammonia giving a low yield of the desired 3b. IR comparison between the material prepared by us and Dhaliwal proved them to be identical. Compound 3b does not melt up to 450°C while 3a shows a melting point of 345°C. This result was not unexpected based on our experience with 1c. Below are tabulated the UV spectra of some pertinent compounds.

Perylene (DMF)	1,3,7,9 Tetraaza-perylene (TCB)	3a (DMF)	3b (DMF) Broad Absorption
λ max 389 nm (ϵ12,166)	λmax 398 (ϵ12,800)	λmax 395 (ϵ7443)	λ390 (ϵ 13,110)
λ max 402 (ϵ26,863)	λ max 415 (ϵ 21,800)	λ max 400 (ϵ7527)	λ410 (ϵ 13,110)
λ max 428 (ϵ35,762)	λ max 434 (ϵ 24,000)	λmax 444 (ϵ16,234)	λ470 (ϵ 5,768)

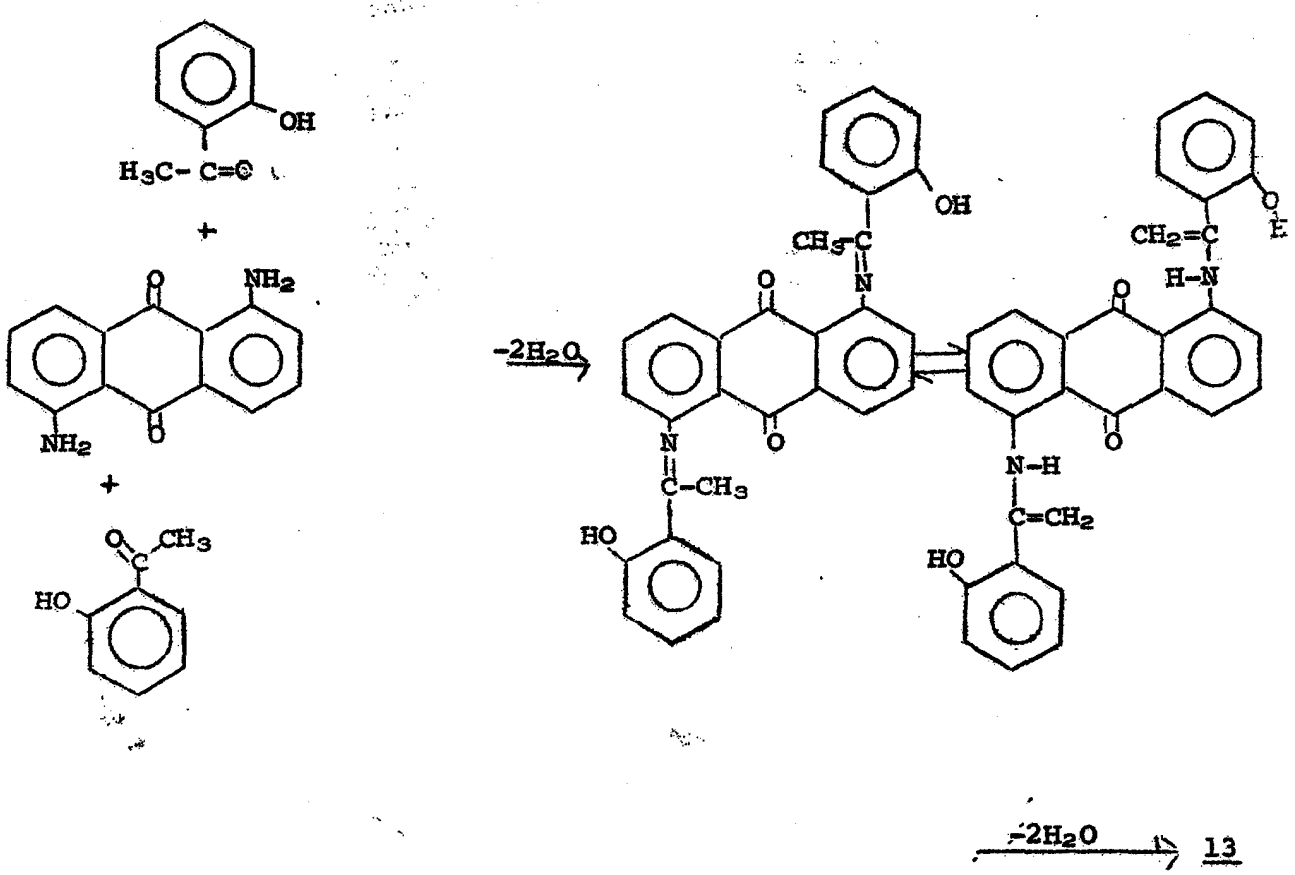
Once again in going from the hydrocarbon perylene to the aza aromatic tetrazaperylene one sees a drop in extinction of the long wavelength absorption and a concomitant bathocromic shift. Similarily the diphenyl tetraazaperylene 3a shows a bathochromic shift and a further drop in extinction vs. tetraazaperylene. Lastly, on going to the di-orthohydroxy perylene 3b one sees an additional drop in extinction and only broad visible absorption. This is a direct parallel to the observation made in the series of compounds 1a,1b,1c.

The lightfastness of yellow compounds 3a, and 3b were determined on materials which were acid pasted and flushed into lithographic varnish. Tint (1/100) and masstones exhibits were prepared and compared against IRgazin 3 RLT. After 71 hours the tint of 3a had completely faded whereas the tint of 3b was only slightly changed. The masstones of 3a, and 3b, however, showed fading of comparable degree. In both cases the standard Irgazin appeared to be superior.

The lightfastness of Compound 3b was somewhat improved when non-particle size reduced material was used in place of acid pasted material However, in neither case was the lightfastness as good as that of compound 1c or 2.

During the course of our work it was noticed that several pigmentary quinazolines derived from anthraquinone derivatives could undergo apparent chemical reduction with the conventional reagent sodium dithionite. It occurred to us that the chemical reduction observed in solution might also be manifest on exposure to light.

To test this idea, a presumably more difficultly reducible compound 13b was synthesized by the condensation of 1,5-diaminoanthraquinone with o-hydroxyacetophenone. The following is a proposed mechanism for the series of reactions leading to 13.



The new yellow compound 13 was prepared in high yield and did not melt up to 425°C. Its structure is based on correct elemental analysis and IR Spectrum which is similar to that of 3b. The lightfastness of this compound was tested on non-particle size reduced material prepared by recrystallization from α-chloronaphthalene. Both tint (1/50) and masstone exhibits were prepared and compared against Irgazin 3 RLT. After 72 hours exposure this material showed some fading in masstone and a slight break in tint. Whereas Irgazin showed very little change. It is not yet established whether compound 13 shows better lightfastness than 3b. The solution spectrum of compound 13 is not yet available but by rubout it appears to have a

sharper spectrum relative to compound 3b. The apparent sharpening in the spectrum of 13 is probably due to the fact that a single conformation is available to the molecule, whereas in 3b isomerism analogous to that in 1c is present.

In the expectation of obtaining a high strength chromophore we synthesized the pero-perylene structure 4a,4b. Since the compound R=o-hydroxyphenyl has not been prepared, the interest in 4 has been restricted to an examination of its visible spectrum. Compound 4a R=methyl displays λ max 410(ϵ 24,650) and λmax 435(ϵ 33,200) in DMF solution. Lightfastness of these compounds have not been determined pending the synthesis of the o-hydroxyphenyl compound for comparison.

The synthesis of a relatively more intense yellow was achieved by the preparation of Compound 5. This material showed λ max 435 nm (ϵ 11,032) in DMF solution. Purified 5 was acid pasted and flushed into lithographic varnish. After 300 hrs. Fadeometer exposure the tint and masstone of 5 showed nearly comparable lightfastness to Irgazin 3 RLT. Although this material displayed reasonably good lightfastness its main drawback is its dull color. The spectrum of this material reveals fairly broad absorption extending as far as 520 nm. In order to see whether the lightfastness of this compound could be further improved and its absorption bands narrowed and shifted to shorter wavelength the related compound 14 has been prepared. This compound shows the expected IR spectrum which is strikingly similar to that of Compound 5 previously prepared and characterized.

The lightfastness of this compound has been evaluated by Fadeometer exposure. The recrystallized crude material was used to prepare tint (1/100) and masstone exhibits which were compared against Irgazin 3 RLT and Anthrapyrimidine yellow. In tint the crude material showed strength comparable to the standards. The new compound is a relatively bright yellow. After 500 hours Fadeometer exposure it showed comparable lightfastness to the standards. The visible spectrum of this material was determined and found to show a λmax at 429 nm (ϵ 19,500). The visible absorption spectrum of this material provides possible evidence that the broadness of absorption seen in o-hydroxyphenylquinazoline molecules may be due to the super imposition of the absorption spectra of the rotomeric isomers. Below is a table of pertinent data.

Spectrum of 14 in DMF Solution		Spectrum of 5 in DMF Solution	
Max	429(ϵ 19,450)	Max	435 (ϵ 11,032)
"	460(ϵ 9,725)	"	460 (ϵ 9,193)
"	480(ϵ 2,650)	"	480 (ϵ 4,413)
"	500(ϵ 90)	"	500 (ϵ 1,323)
"	520(ϵ 0)	"	520 (ϵ 514)

As the table shows compound 5 has approximately 1/2 the extinction of compound 14 at its maximum. Thus possibly implying that compound 5 is existing in two distinct rotomeric forms. The sharper drop in extinction in compound 14 also supports this point since this is what would be expected of a molecule confined to only one conformation i.e. it shows a sharper absorption maximum.

In order to test the idea that an ortho-hydroxyphenylquinazoline moiety could improve the lightfastness of an otherwise marginally lightfast pigment, a direct comparison between structure 7 and its commercial counterpart Anthrapyrimidine yellow was desirable.

The synthesis of 7 started with the hyrolysis of yellow compound 5 to give the red amine 6. Although 6 was not obtained in completely pure form its structure is supported by its IR spectrum which shows an amine doublet and a conjugated carbonyl band. Conclusive proof of structure was achieved by its conversion to Compound 3b by simple heating with salicylamide. Compound 7 is an insoluble dull yellow which did not analyze within acceptable analytical limits after acid recrystallization. However, its IR spectrum is very similar to its analog Anthrapyrimidine yellow.

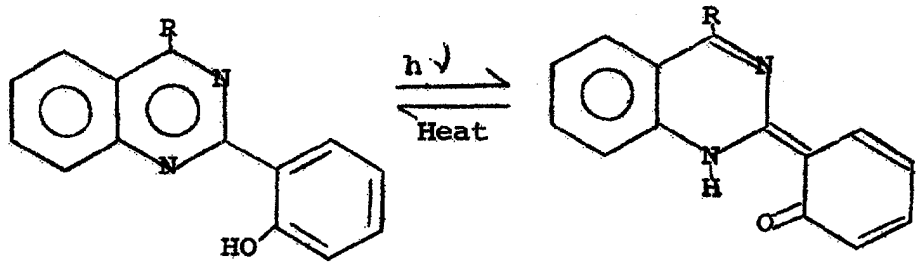
The lightfastness of 7 was determined on crude acid recrystallized material. Tints (1/100) and masstone exhibits were prepared and compared against Anthrapyrimidine yellow. After 72 hrs. Fadeometer exposure this material showed significant darkening in masstone and tint whereas, Anthrapyrimidine yellow remained unchanged. The results were disappointing and did not demonstrate that an o-hydroxyphenylquinazoline moiety could improve the lightfastness of an otherwise insufficiently lightfast pigment.

The availability of Ciba Chromophthal Red 3B enabled us to prepare yellow compounds 8a,8b. In (DMF) solution the visible spectrum of compound 8a showed λ max 430 nm (ε 8364). In contrast the visible spectrum of the ortho-hydroxyphenyl analog 8b showed only broad absorption, the maximum extending from 420 nm (ε 4263) to 440 nm (ε 4263). Once again we see a broadness of absorption with a concommitant drop in extinction coefficient on going from the phenyl analog to the ortho-hydroxyphenyl derivative.

The lightfastness of compounds 8a and 8b were determined. Compound 8b X=OH showed somewhat better lightfastness than the phenyl derivative when it was evaluated in crude form. However, both compounds showed better lightfastness than compound 3b and comparable photostability to 1c and 2 thus suggesting that a greater delocalization of electrons over a more extended aromatic system is detrimental to the photostability of the quinazolines type compounds.

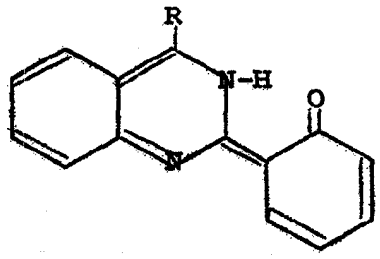
Proton Transfer in Quinazolines

In 2- ortho-hydroxyphenyl)quinazoline it is known that the molecule exits in the conformation C shown below. This is also the conformation from which a proton is transferred on photoexcitation.



C

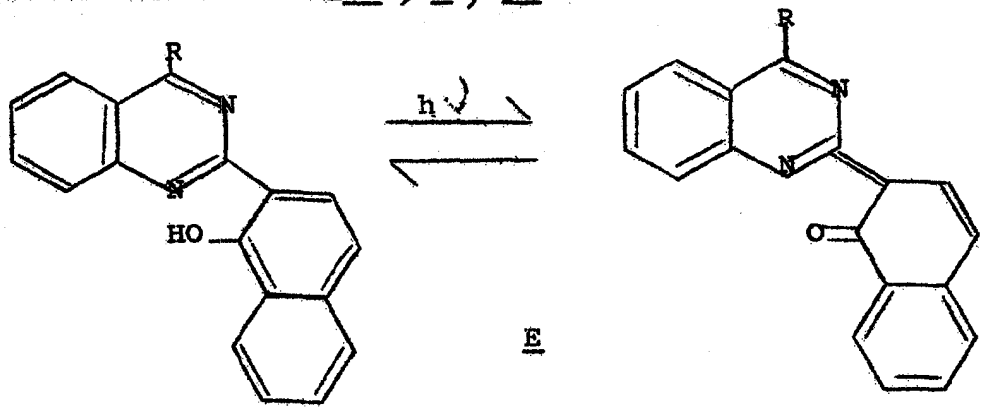
The alternative to conformation C would be conformation D in which the proton would be transferred to the nitrogen at position three.



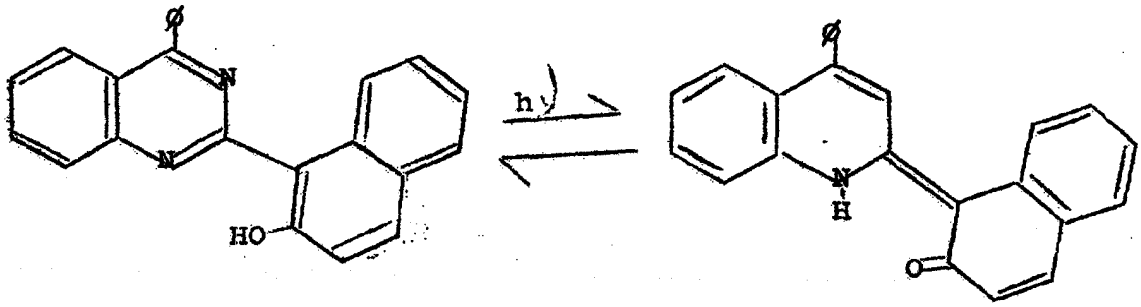
D

In C the loss in resonance energy of the heterocycle on photoexcitation is smaller than in D. Conclusive proof that conformation C is the preferred one has come from NMR spectroscopy of various substituted quinazolines. It is known that the photostabilities of 2-ortho-hydroxyphenylazaheterocycles, results from the photoenolization mechanism shown. The greater photostabilities ought to be associated with heterocycles undergoing the least change in resonance energy on proton transfer.

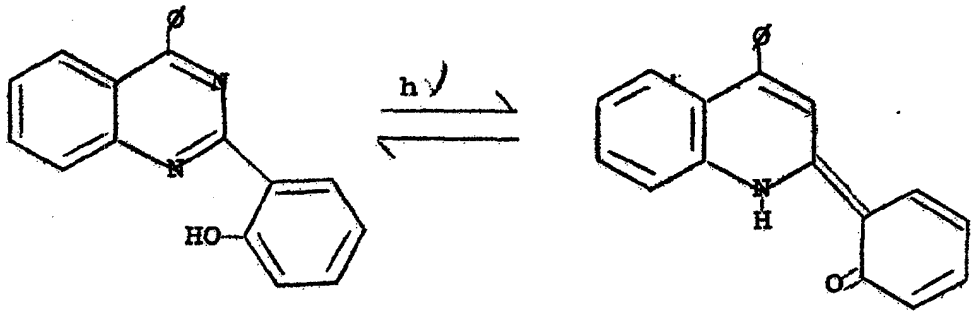
γ It appeared that this point could be demonstrated by varying the nature of the phenolic portion of the 2-substituted quinazoline. Thus the predicted order of photostability for the following four compounds should be E ≃ 11 > 9 > 10



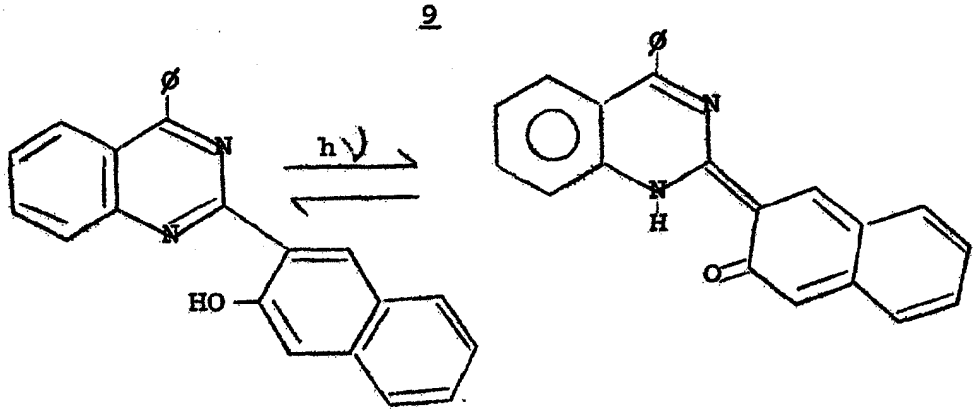
E



11



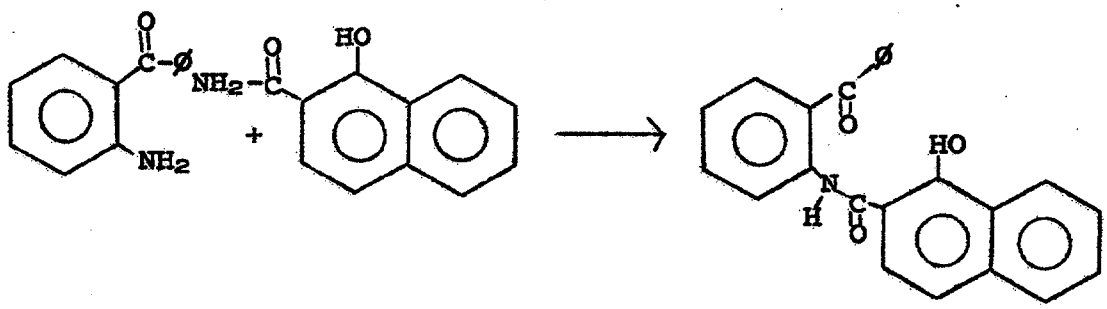
9



10

That is, the molecule which loses the least amount of resonance energy on excitation should be the most photostable. It has also been shown that the position of the phenolic OH signal in the NMR spectrum is proportional to the electron density on Nitrogen #1. This has been corroborated in a series of substituted 2-(ortho-hydroxyphenyl)quinazolines . Therefore, it is possible that the position of the OH signal in the NMR will be a function of the photostability of these compounds. Compounds 10 and 11 were prepared via the previously described synthesis. It is interesting that the preparation of E could not be achieved by this synthesis using 1-hydroxy-2-naphthalamide. The product of this reaction was

only the amide 17, shown below.



17

The position of the OH resonance of compounds 9,10,11,12 are tabulated below.

COMPOUND	δ(OH) $CDCl_3$/(TMS)	δ (OH)$CDCl_3$/(TMS)
9	13.16 ppm	phenol 2.8 ppm
10	13.66	β Naphthol 3.2
11	very broad absorption above 8ppm	
12	13.91	

The results indicate that the ordering of the signal positions are not as expected. It was expected that the signal for 10 would have appeared below δ 13.16 since in this compound the acidity of the OH proton was expected to be lowest. In contrast, the position of the resonance for 12 may be reasonable in view of the fused benzene ring.

The broad absorption observed for the OH signal in compound 11 is surprising. This broadness may indicate restricted rotation about the bond connecting the quinazoline and naphthalene portions of the molecule. This point ought to be demonstratable from the UV spectrum of this compound.

In a paper by Porte et al, (J.A.Chem.Soc. 82,5057 (1960)),the chemical shifts at infinite dilution of various hydrogen bonded phenols were recorded. They observed that a linear correlation existed between the position of the OH resonance in the NMR and the C=O frequency in the IR spectrum. Their results showed that internally hydrogen bonded phenols had the OH signals quite downfield from the non-hydrogen bonded simple phenols. (8-11ppm). So in comparing compounds 9,10,11,and 12 to phenol and β Napthol one sees the expected large downfield shift of the OH resonance.

The UV Spectra of Compounds 9,10, and 11 are given below.

Compound	UV Max*	(ε)
9	330 nm	12,000
10	Sh(350)	10,250
	310	28,700
	270	48,700
11	355	10,300
	315	14,250

* In DMF Solution

In comparing 9,10, and 11 we see a bathochromic shift in the long wavelength absorbtion of 10 and 11 relative to 9. This is reasonable since we are presumably extending the conjugation of the system relative to compound 9. The lack of absorption bands in 11 vs. 10 and the decrease of extinction of 11 is indicative of a decrease in conjugation of 11. However, this argument is not conclusive since, we do not have the compounds lacking the hydroxyl groups for comparison. The availability of the non-hydroxylated derivatives would enable us to differentiate between a substituent effect due to the hydroxyl group and the effects due to conformation. However, the evidence presented above does in fact suggest that compound 11 is twisted.

Evaluation

The following compounds have been incorporated into clear lacquer and drawn down over a clear transparent film: 9,10,11,12, and 15. The material 15 was included so as to determine its photostability and relate it to that of the pigments based on this heterocycle such as 13, and 14.

After 92 hours the following order of photostabilities were noted. The ratio of the initial absorption Ao at the maximum to the final absorption A are recorded. The order of photostabilities are as follows:

λmax 340 nm	λmax 330	λmax 355	λmax 355	λmax 305
12, A/Ao = 1	9, A/Ao = .97	11, A/Ao = .5	15, A/Ao = .3	10, A/Ao = .13

Since it was observed that experimental material 12 and 9 had comparable photostability, they were submitted for Fadeometer exposure for a full 500 hours. The following results were noted.

12, A/Ao = .914 9, A/Ao = .894

Compound 12 actually shows better photostability than 9.

In comparing the photostabilities of 12 to 9 it would appear that free rotation of the phenyl ring in 9 does not contribute to the deactivation of the excited singlet state of 9.

Our results are somewhat disappointing in that the ordering of photostabilities are not what one could have expected based purely on resonance energy considerations. The fact that compound 10

is least stable is reasonable but the fact that compound 11 is not the most stable is unexpected. The observation that compound 15 shows reasonable photostability correlated well with our observation of the related yellow pigment 14.

Violet Perinone 16

The availability of 1,4,5,8 tetraaminonaphthalene prompted us to prepare violet perinone 16. The material was acid recrystallized presumably isolating one of the two possible isomers and evaluated for lightfastness. Tints and masstones were prepared and compared against RT-795-D. After 350 hours Fadeometer exposure 16 displayed comparable lightfastness to the quinacridone standard.

Conclusions

Various ortho-hydroxyphenylquinazoline pigments have been prepared. In most cases an improvement in lightfastness is observed with the introduction of an ortho-hydroxyphenyl moiety relative to a phenyl group. The lightfastness of certain derivatives (1c,2,5,8b) is improved over others. (3b). In terms of color many of these compounds show absorption spectra which are too broad to be of interest tinctorially. This result has been modified in the mono-aza derivatives exemplified by compound 14.

Experimental

The pertinent technical data is to be found in laboratory Note-book 1926K.

Synthesis of 3b - NB 1926/100

Into a 4 neck mechanically stirred reaction vessel was charged 78 grams (0.328 mole) commercial 1,5-diaminoanthraquinone and 650.0 grams salicylamide and the mixture blanketed with nitrogen. After the ingredients were well mixed, 6 ml of nitrobenzene was added to avoid plugging the reflux condenser. The reaction mixture was melted and eventually brought to reflux (250°C). The mixture was homogenous and on continued heating began to evolve water. On heating for about 10 minutes crystals of compound 3b appeared to precipitate out of the melt. After the reaction was complete the mixture was cooled to 150°C and 500 cc (DMF) was added. The mixture was refluxed for 15 minutes and the solid filtered hot. The yellow material was washed with DMF and then methanol, yielding 122 grams (84.6%) of 3b. The solubility of this material is about 1g in 2 liters boiling nitrobenzene. The highest quality material can be obtained by acid recrystallization from sulfuric acid followed by solvent recrystallization.

Synthesis of 13 - NB 1926/168

Into a 4 neck mechanically stirred reaction flask was placed 3g 1,5-diaminoanthraquinone and 25cc 2-hydroxyacetophenone. The mixture was blanketed with nitrogen and heated to reflux (220°C), at which point the reaction mixture was homogenous. The mixture was refluxed for 24 hours. The heavy slurry of product was diluted with α-chloronaphthalene and maintained at 150° for 10 minutes, and the

solid filtered and washed free of solvent, yielding 5.25 gr of 13. This material can be recrystallized from α-chloronaphthalene. Its solubility is 4g/liter of boiling α-chloronaphthalene.

Analyses - All compounds the analyses of which are given below, appear in notebook 1926K and their page numbers are recorded below.

P.62,86-1b calcd for $C_{24}H_{14}N_4$:C,80.43; H,3.94; N,15.63
Found: C,80.2; H,4.4; N,15.8

P.48-1c calcd for $C_{24}H_{14}N_4O_2$: C,73.84,H,3.61;N,14.35
Found: C,73.9;H,3.8;N,14.5

P.94-2 calcd for $C_{28}H_{16}N_4O_2$: C,76.35; H,3.66; N,12.72

Found: C,76.3,; H,3.9,N,12.9

P.71-3a calcd for: $C_{28}H_{16}N_4O_2$; C,76.35; H,3.66;N,12.72

Found: C,76.0; H,3.8; 12.7.

P.100-3b calcd for: $C_{28}H_{16}N_4O_2$; C,76.35; H,3.66; N,12.72

Found: C,76.0; H,3.8; 12.7

P.163-3c calcd for: $C_{28}H_{12}Cl_4N_4O_2$; C,58.2; H,2.095; N,9.7;Cl,24.5

Found: C,56.5; H,2.3; N,8.5; Cl,23.6

P.108-4a calcd for: $C_{24}H_{14}N_4$; C,80.43; H 3.94; N, 15.63
Found 80.5; H,4.1; N,15.1

P111-4b calcd for: $C_{34}H_{18}N_4$; C,84.63; H,3.76; N,11.61

Found: C,83.0;H,3.7; N,11.5

P.93-5 calcd for: $C_{28}H_{17}N_3O_2$; C,75.84; H,3.86; N,9.48

Found: C,75.9; H,4.0; N, 9.6.

P.116-Crude 6 calcd for: $C_{21}H_{13}N_3O_2$; C,74.33; H,3.86; N,12.38
Found: C,68.3; H,3.9; N,11.5

P.152-7 calcd for: $C_{37}H_{19}N_5O_4$; C,74.37; H,3.2; N,11.72

Found: C,68.1; H,3.3; N,10.6.

P.65-8a calcd for: $C_{42}H_{22}N_4O_2$: C,82.6; H,3.61; N,9.12
Found: C,80.0; H,4.0; N,9.0

P.124-8b calcd for:$C_{42}H_{22}N_4O_4$ C,78.1; H,3.40; N,8.66
Found: C,77.2; H,3.5; N,8.2

Compound 9 - has been previously prepared and had acceptable analysis.

P.115-10 calcd for: $C_{24}H_{16}N_2O$: C,82.74; H,4.63; N,8.04

Found: C,81.6; H,4.7; N,7.8

P.167-11 calcd for: $C_{24}H_{16}N_2O$: C,82.74; H,4.63; N,8.04

Found: C,82.8; H,4.7; N,8.05

P.96-12 calcd for: $C_{20}H_{12}N_2O$: C,81.07; H,4.08; N,9.45

Found: C,81.0; H,4.3; N,9.5

P.168-13 calcd for: $C_{36}H_{18}N_2O_2$: C,82.18; H,4.14; N,6.39

Found C,82.1; H,4.3; 6.4

P.171-14 calcd for: $C_{29}H_{18}N_2O_3$: C,78.72; H,4.10; N,6.33

Found: C,78.7, H,4.3; N,6.3

P.183-15 calcd for: $C_{21}H_{15}NO$:C,84.82; H,5.08; N,4.71

Found: C,84.4; 5.0; N,4.7

P.165-16 The following analysis pertains to either cis to trens. 16 obtained by acid recrystallization of the crude product.

calcd for: $C_{26}H_4N_4O_2Cl_8$: C,45.45; H, 0.582; N,8.16; Cl,41.2

Found: C,44.9; H,0.7; N, 8.2; Cl,39.4

P.114-17 calcd for: $C_{24}H_{17}NO_3$; C,78.46; H,4.66; N,3.81

Found: C,78.7; H,4.7; N,3.9

UV Spectra - See NB 1961

1a UV Max (DMF) 300 nm (11,574),311(12,324),344(2,577),361(4,967), 375 sh(4,615),381(6,677).

1b UV Max (DMF) 293(81,124),421(3,136)

1c UV Max (DMF) 285(83,025) 358(37,739)

2 UV Max (DMF) 254(33,484),276(56,014),343 sh (35,970),362(42,340)

3a UV (DMF) 260(47,785), 272(52,606),344(8,288),395(7,443),400(7,527), 418(12,686),444(16,239)

3b UV Max (DMF) 267(70,794),320(33,561)

4a UV (DMF) 277(51,000),305 sh (24,000),385(20,600),410(24,650), 435(33,200)

5 UV (DMF) 265 (50,896); 435(11,032)

8a UV (DMF) 288(83,643), 351 sh (13,334)

8b UV (DMF) 268(32,401),288(38,796),315(34,106),358(14,779)

12 UV (DMF) 266(32,900), sh 272(31,650), sh 300(18,500),sh 342(8760), sh 387(4,880)

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