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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Derivatives of Squaric Acid

Period Covered (Part Time) October 1969 - January 1971

FILE: 223

DATE: 3/12/71

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

SUBJECT: Derivatives of Squaric Acid

PERIOD COVERED: (Part Time) October 1969 - January 1971

SUBMITTED BY: Lawrence R. Lerner Date Submitted: 1/18/71

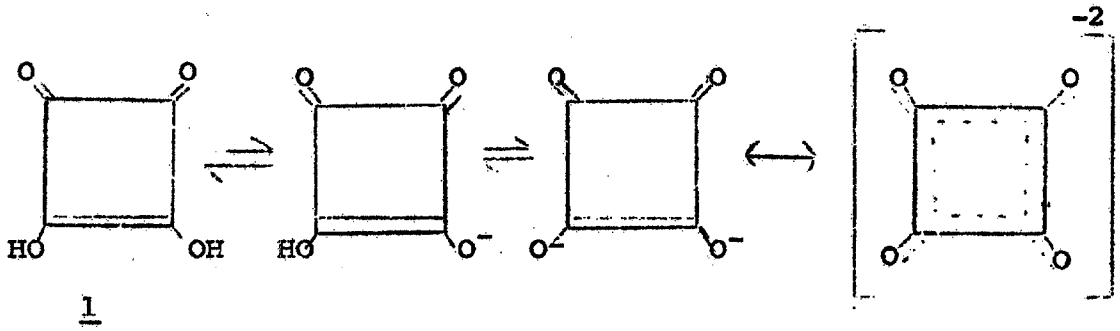
APPROVED BY: E. E. JAFFE Date Released: 3/12/71

ABSTRACT

Squaric Acid has been substituted in the 1,3-positions with a variety of nucleophilic reagents. Many of the products are characterized by extremely high extinction coefficients (mostly blues) and generally poor lightfastness. Others in the yellow to orange range show less strength but promising lightfastness.

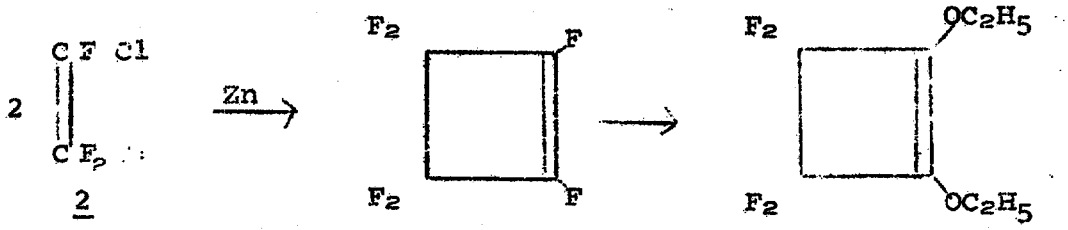
I. Introduction

Squaric Acid (3,4-dihydroxycyclobutenedione), 1, a colorless, strongly acidic material (pk_2=2, pk_1 ~1), was first prepared in 1959[1]. It has been suggested[2] that the dianion has considerable aromatic character, and this aromaticity provides the driving force for ionization.



1

Squaric Acid was originally prepared[1,3] from chlorotrifluoroethylene (2) as fcllows:



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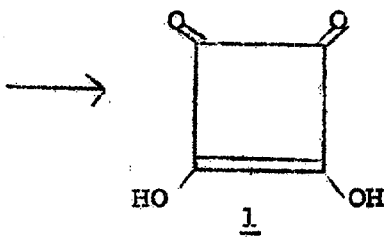
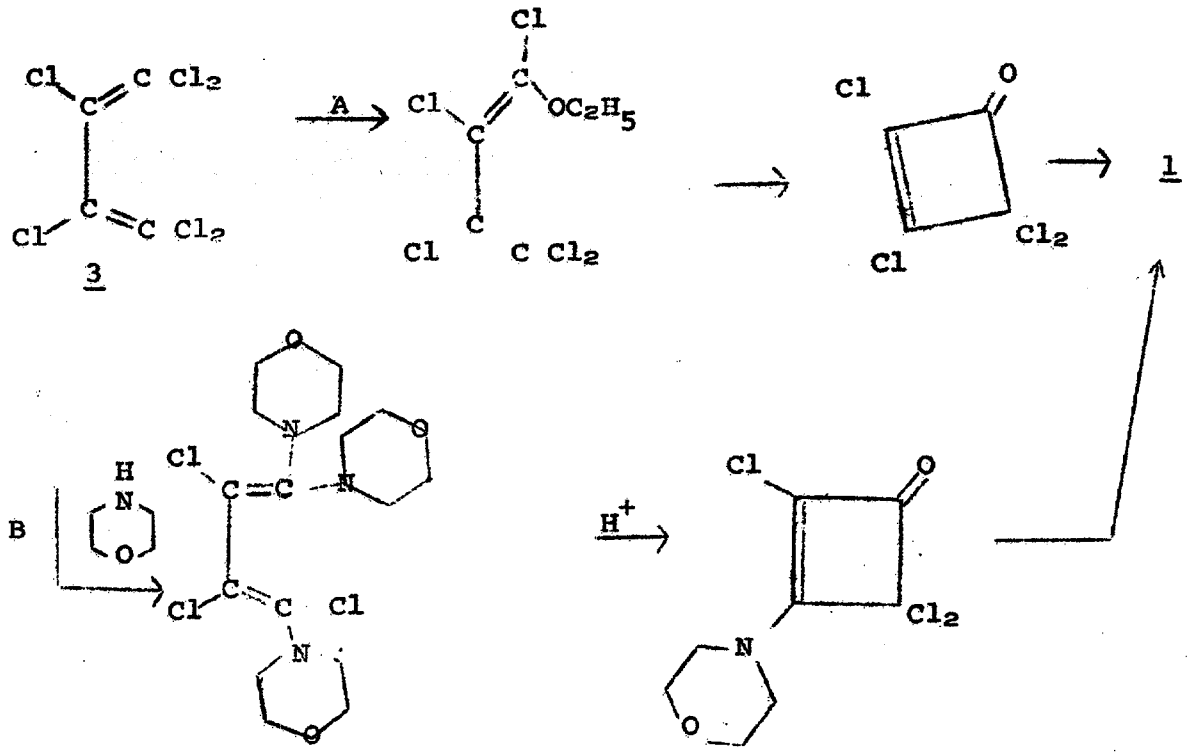
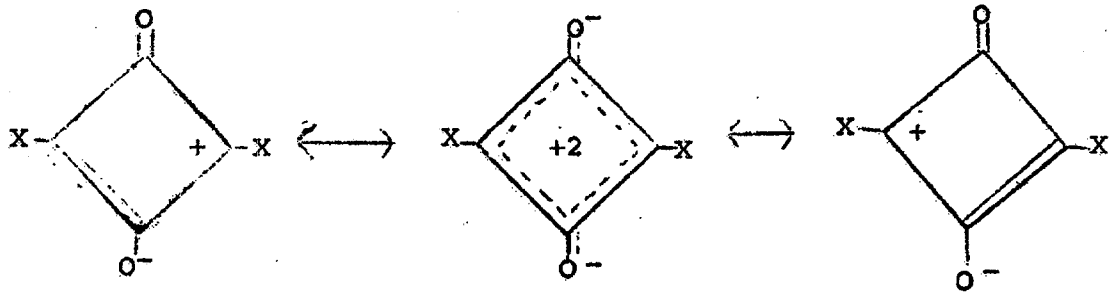


1

More recently a German firm has reported[4] a commercial synthesis starting with hexachlorobutadiene (3). The reaction is carried out in one step (route B) without isolation of the intermediates.



Squaric Acid undergoes many reactions, but this report will be limited, in general, to products formed by reaction with nucleophilic reagents to produce 1,3-substituted "squarates", 4,(cyclobutenedione diolates or cyclobutenediylium diolates) with pigmentary potential.



4

The interested reader can consult recent review articles[4,5], for additional information.

II Summary and Conclusions

1. 48 different derivatives of Squaric Acid have been prepared and evaluated in the Fadeometer.

2. Only two made, thus far, warranted further testing and are out on Florida exposure in TAE-3.

a. The orange product derived from barbituric acid,

b. The orange product derived from 2-aminofluorenone.

III. Patent Status

As none of these compounds is of commercial interest at this time, no work has been done toward establishing novelty and utility for a patent application.

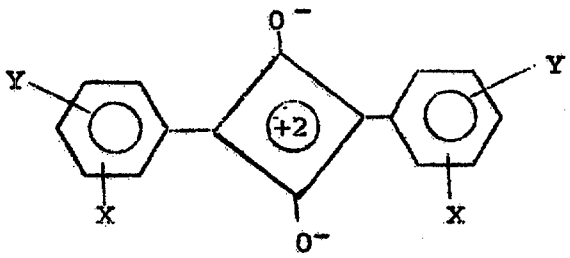
IV. Discussion

Substituted Benzene Derivatives

These compounds are, generally, blues of extreme strength (some having molar extinction coefficients of greater than 200,000 in solution). They also show some solubility in polar solvents and relatively poor lightfastness. They are easily prepared by reacting stoichiometric amounts of the activated aromatic compound with squaric acid in acetic acid or a mixture of 1-butanol and benzene (azeotropic removal of water). None of these compounds seemed to be of further interest due to the color (blue) and relatively poor lightfastness. Table I summarizes the results found with each compound.

TABLE I

SUBSTITUTED BENZENE DERIVATIVE OF SQUARIC ACID



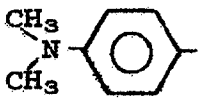
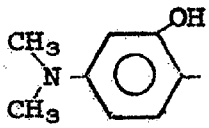
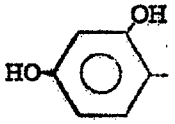
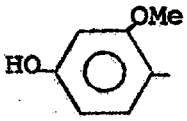
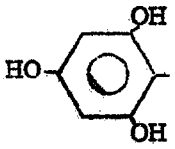
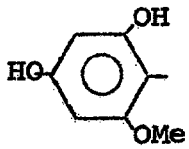
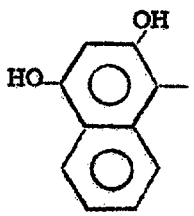
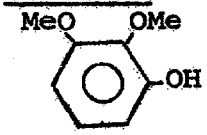
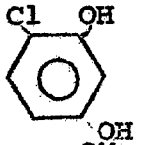
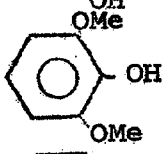
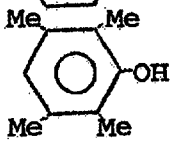
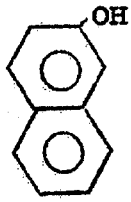
AROMATIC COMPOUND	EXP.NO.	COLOR	FADEOMETER	COMMENTS
	1921/27	Blue	Tint:fade 24 hrs. Mass: dark-ens	Purchased from Aldrich Chemical Co.
	1937/7	Blue	Tint:fade 72 hrs. Mass:dark-ens	OH group may improve lightfastness
	1921/56	Violet EtOH λmax. 573 (200,000)	Tint:fade 100 hrs. Mass:dark-ens	Soluble but relatively good lightfastness poor yield in prep.
	1921/60	Violet DMSO λmax. 583		Very poor yield. not fully characterized; appears to fluoresce
	1921/48	Blue $CHCl_3$ λmax.586 (153,000)	Tint:fade 200 hrs. Mass:dark-ens	Soluble but relatively good lightfastness
	1921/59	Blue DMSO λMax.586 (132,000)	Tint:fade 200 hrs. Mass:dark-ens	Relatively soluble; relatively lightfast
	1937/46	Blue	Tint:fade 24 hrs. Mass:slight change	Conjugation does not aid lightfastness

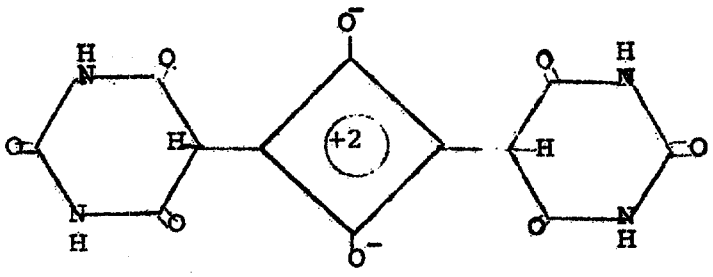
TABLE I CONTINUED

AROMATIC COMPOUND	EXP.NO	COLOR	FADEOMETER	COMMENTS
	1921/51			No reaction;not sufficiently nucleophilic
	1921/52			"
	1921/53			"
	1921/61			"
	1921/71			"
	1921/79			"

Products From Activated Methylene Compounds

These compounds are hypsochromically shifted relative to the benzene derivatives (less conjugation). They also show decreased strength, but in some cases, lower solubility and enhanced lightfastness.

The procedures for preparing these compounds are the same as those previously discussed. One compound of particular interest is the insoluble orange product formed from barbituric acid (5) which has been mentioned briefly in the literature[5]. In ZnO extension, it shows



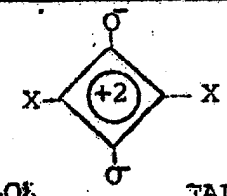
5

a slight change initially (24 hrs.) but after 300 hrs. still retains most of its color. It looks fair after 508 hrs., but the masstone shows only a slight change. Though it does not have the strength of the benzene substituted compounds, it is still quite strong (λ^{DMF}_{max} 492;60,000).

A sample is out on Florida exposure in thermosetting acrylic enamel (TAE-3). Table II summarizes the results found with these compounds.

TABLE II

PRODUCTS FROM ACTIVATED METHYLENE COMPOUNDS AND SQUARIC ACID



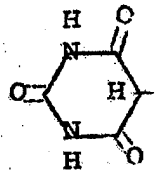
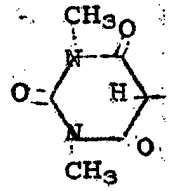
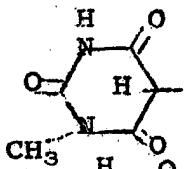
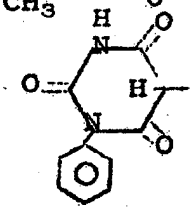
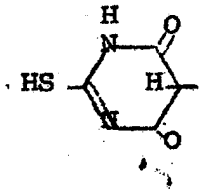
X	EXP. NO.	COLOR	TADEOMETER	COMMENTS
	1921/32	Orange DMF λ_{max} 492 (60,000	Tint and masstone: good 300 hrs.	Turns brown upon dispersion milling. See discussion section for further information
	1921/69	Orange DMSO λ_{max} 499 (94,000)	Tint and masstone: severe fade 24 hrs.	Soluble and very poor lightfastness. Both due to lack of intermolecular H-bonding?
	1937/57	Orange	Tint and masstone: slow fade 24 hrs. and up	Fair elemental analysis intermediate solubility, intermediate lightfastness.
	1937/47	Orange	Tint and masstone: fade in 24 hrs.	Fairly soluble poor lightfastness
	1937/14	Purple	Tint-fades 24 hrs.	Soluble

TABLE II CONTINUED

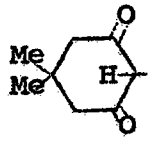
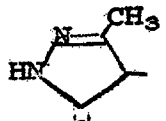
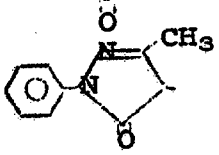
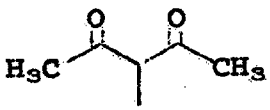
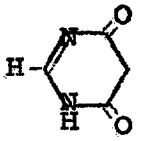
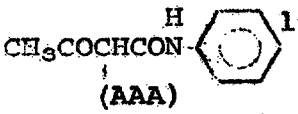
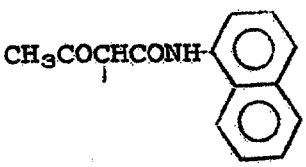
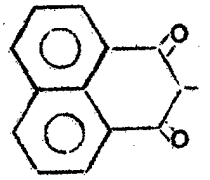
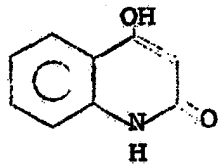
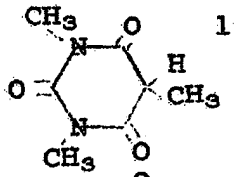
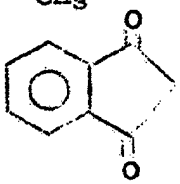
X	EXP. NO.	COLOR	FADEOMETER	COMMENTS
	1937/8			Soluble in reaction medium; orange solution
	1937/37	Dull Orange	Tint and Mass: Fade 24 hrs.	
	1937/35	Violet	Tint and Mass; severe fade 24 hrs.	
	1937/34			Soluble in reaction medium; dark red solution
	1937/20	Brown		Poor yield; not further characterized
 (AAA)	1921/42	Colorless		Get off 2x theoretical amt: of water. Very insoluble, structure unknown
p-nitroAAA	1921/50	Yellow Ochre	Tint:fade 24 hrs. Mass: darkens	Unknown structure
	1937/40	Pale Yellow		Poor yield unknown structure

TABLE II (CON'T)

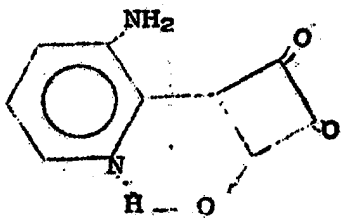
X	EXP NO.	COLOR	FADEOMETER	COMMENTS
ØNHCOCHCONHØ |	1937/61	Pale gold	Mass and tint: fade 24 hrs.	Gives good elemental analysis for 2:1 adduct
	1937/50			No reaction in AcOH or butanol/ benzene
	1921/40			No reaction under a variety of conditions
	1921/70			No reaction
	1921/63			Products soluble in reaction medium; at least 4 major products (TLC)

Substituted Aniline Derivatives

The third class of compounds prepared can be considered derivatives of aniline, where the amino group behaves as the nucleophile upon reaction with squaric acid[5,6,7]

These compounds range in color from pale yellow to orange. Most (with notable exceptions) are relatively soluble and show poor lightfastness. There was one unusual 1:1 adduct found in this series which will be discussed first.

It has been reported[5] that 3- aminopyridine forms a 1:1 adduct (6) instead of the usual 2:1 product.

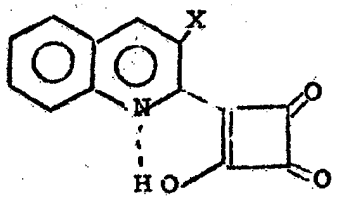


6

This compound was found to be insoluble (1921/43) and high melting (> 320°C), but has most of its absorption in the UV, (λ_{max}^{DMF} 400 (14,000). A few quinoline derivatives were prepared, but either were not strong enough or showed poor lightfastness. Table III summarizes these results.

TABLE III

1:1 ADDUCTS OF SQUARIC ACID

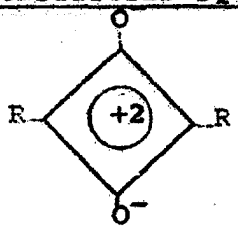


X	EXP. NO.	COLOR	FADEOMETER	COMMENTS
$-NH_2$	1937/2	Red-yellow	Tint:fade 72 hrs. Mass:darkens 96 hrs.	DMF insoluble tint and mass: show some color after 168 hrs.
nickel chelate of above	1937/15	Green-yellow	Tint:fades 24 hrs. Mass:darkens 24 hrs.	
$NHCOCH_3$	1937/9	Pale yellow	Mass:fades 90 hrs.	Relatively poor elemental analysis
OH	1937/12	Pale green-yellow		Not "rubbed" out

The results found with the "normal" 2:1 aniline derivatives, with the exception of the "keto" compounds are shown n table IV.

TABLE IV

ARYLAMINO SUBSTITUTED SQUARIC ACID



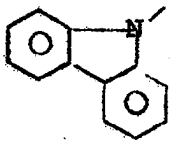
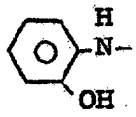
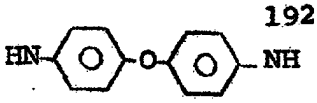
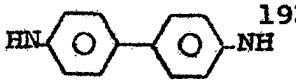
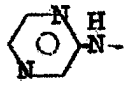
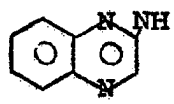
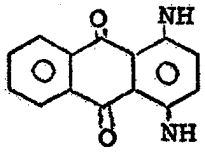
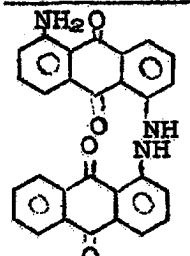
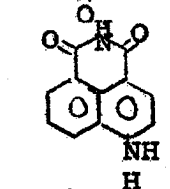
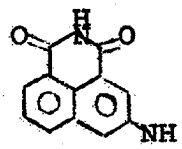
X	EXP. NO.	COLOR	FADEOMETER RESULTS	COMMENTS
	1921/34	Orange DMF λmax 497(64,000)		Very soluble and high melting (368-370°, decomp.)
	1921/37	Pale green-yellow	Tint:fades 24 hrs. Mass: darkens	Fairly soluble
	1921/38	Green-yellow	Tint:fades 24 hrs. Mass: darkens	polymeric m.p.> 470° (darkens 350°)
	1921/39	Red-yellow	Tint:fades 24 hrs. Mass: darkens	Polymeric m.p. > 470° (darkens 270°)
	1937/52	Green-yellow	Tint:fades 24 hrs. Mass: slight change	
	1937/53	Green-yellow	Tint:fades 24 hrs. Mass: darkens	
	1937/54	Yellow		DMF soluble m.p.210-220° (decomp)
	1937/5	Blue-gray	Tint: fade 24 hrs. Mass: no apparent change	Polymeric m.p.> 450°

TABLE IV CONTINUED

Y	EXP NO	COLOR	FADEOMETER RESULTS	COMMENTS
	1937/6	Dull violet	Tint:fade 24 hrs. Mass: slight fade	Polymeric m.p. 450°
	1949/15	Brown		Not further investigated
	1949/8	-	-	No reaction
	1949/16	Dull yellow	Tint:fades 24 hrs. Mass: fades 24 hrs.	Poor analysis

A series of acetophenone, benzophenone and fluorenone derivatives were prepared and showed interesting physical properties, summarized on Table V.

TABLE V

KETO ARYLAMINO DERIVATIVES OF SQUARIC ACID

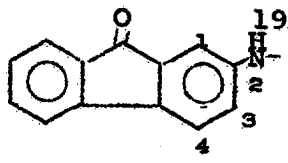
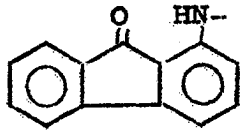
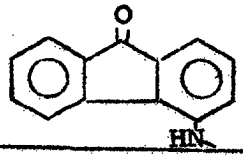
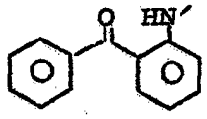
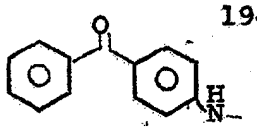
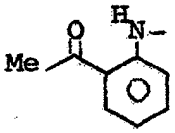
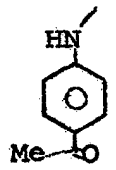
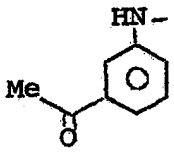
	NB No	I.R. Carbonyl Frequency 1= lowest	Color	10-best 1-color gone 24 hrs.	Comments
	1937/78	2	Orange	10	Very insoluble fairly good lightfastness 407 hrs.
	1937/77	1	Orange DMF max. 483 (38,000)	7	Still some color after 407 hrs. in Fadeometer
	1949/17	2	Yellow	2	Recrystallized from DMF

TABLE V CONTINUED

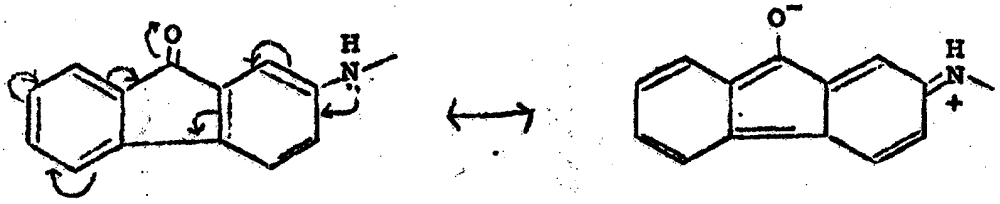
	1949/6	1	Red-yellow	5	Recrystallized from DMF. Some color after 147 hrs. in Fadeometer
	1949/18	2	Green-yellow	1	Not recrystallized but showed good elemental analysis
	1949/10	1	Red-yellow solid DMF $\lambda_{max.}$ 450(40,000)	4	Fairly soluble DMF recrystallized
	1949/9	2	Green-yellow solid DMF $\lambda_{max.}$ 442(35,000)	3	Soluble DMF recrystallized
	1949/19	3	Green-yellow	1	Soluble DMF recrystallized

It should be noted that within each group (excluding, for the moment, 2-aminofluorenone), the compound with the lowest frequency I.R. carbonyl band (lowest energy) is the one having the carbonyl adjacent to the nitrogen. These correspond, as well, to the more photostable compounds. This behavior is analogous to that found in classical solution photochemistry[8]. In solution, it has been shown that reversible hydrogen transfer helps prevent photoreduction (intramolecular H-bonding; also leads to lowering of carbonyl frequency) and a similar mechanism might be postulated here. The para-substituted materials can be stabilized via electron donation from nitrogen to the carbonyl, with which it is conjugated. This explanation also has precedent in classical solution photochemistry. The meta-substituted compounds cannot be stabilized in either way and in all but one case show the poorest photostability.

The compound which appears to be anomalous is the product from 2-aminofluorenone (call 2AF). A clue to its enhanced photostability may lie in its bathochromically shifted color vs. the other meta-substituted fluorenone (4-aminofluorenone) derivative; orange, as

opposed to yellow.

Though in 2AF direct conjugation between the nitrogen and the carbonyl is absent, conjugation can occur via the other fused benzene ring as shown:



This extended conjugation might account for the orange color and possibly a less energetic (less reactive?) excited state. The aceto- and benzophenones cannot have this type of conjugation, and thus, photostabilization. Another mode of stabilization, instead of, or in addition to, the first is intermolecular hydrogen bonding. Compound 2AF may be able to pack in the crystal lattice in such a way as to maximize intermolecular H-bonding and thus maximize photostability via reversible intermolecular hydrogen transfer.

A large sample of 2AF is out on Florida exposure in thermosetting acrylic enamel (TAE-3).

V. Experimental

Experimental details can be found in the references included in the tables.

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1. S. Cohen. J.R.Lacher, and J.D.Park, J.Amer.Chem.Soc., 81, 3480(1959).

2. S.W.Tobey, and R.West, Tetrahedron Letters, 1179(1963).

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6. G. Manecke and J. Gauger, Tetrahedron Letters, 3507(1967); 1339 (1968).

7. J. Gauger and G. Manecke, Chem.Ber., 103, 2696(1970).

8. For example see: N. Turro, "Molecular Photochemistry", W.A.Benjamin Inc., New York, 1967, pp 137-154.