

“NAPHTHANIL” COUPLING COMPONENTS: RELATIONSHIP
BETWEEN CHEMICAL STRUCTURE AND
CELLULOSE SUBSTANTIVITY

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Received March 9, 1953

INTRODUCTION

This paper deals with studies on the relationship between cotton substantivity and the aryl amides of 3-hydroxy-2-naphthoic acid and other aromatic *o*-hydroxycarboxylic acids which are known in the trade as “Naphtol”, “Naphthol”, “Brenthol”, or “Naphthanil” coupling components. Insoluble azo dyes are generated from these components in the fibers by impregnating or adsorbing a caustic soda solution of these almost colorless phenolic compounds on cotton, followed by treatment with diazo compounds.

In most applications, the affinity of the sodium salts of the aryl-amides for the cellulose fiber is a significant and controlling property. To meet requirements for various uses in the trade, arylamide products varying from low to high substantivities have been developed. For dyeing purposes, particularly in machine dyeing, and where a high fastness to rubbing is required in the final color, a highly substantive arylamide is needed; and for printing purposes, where the component is padded, a low substantivity is preferred so that soaping will readily remove the undeveloped component and leave a clear, white pattern (1-3).

All of the arylamides in commercial use display some degree of affinity for cotton; but there are wide variations in the substantivity (% exhaustion from dye bath solution) which range from 10 to about 75%. These variations in affinity appear to be dependent, to some extent, on the chemical constitution of the arylamide. The structural features of the arylamides and their influence on cotton substantivity have, therefore, been subject to considerable investigation. It is obvious that the more clearly the relation between constitution and substantivity is understood, the more easily can products be prepared possessing certain and definite properties.

The substantivity of many arylamides has been determined by gravimetric methods either directly by nitrogen analysis of the impregnated cotton, or indirectly by acid precipitation of the residual arylamide left in the bath after exposure to the cotton fiber (1, 4-9). More recently methods have been described for colorimetric determination, by either ultraviolet light on the residual arylamide left in the bath, or visual light on water-soluble colors formed by coupling with diazo components (10-12).

The subject arylamides have been classed generically with direct cotton dyes which are positively absorbed by cellulose, even though they do not generally possess that elongated structure which characterizes most of the known direct cotton dyes.¹ Certain of the arylamides possess considerable substantivity and

¹ Types of molecule substantive to cellulose which are derived from benzidine, dianisidine, *p, p'*-diaminostilbene, 1,4-diaminonaphthalene, etc.

their absorption on cotton follows a course similar to a quickly diffusing dye (13, 14).

In the arylamides of the *o*-hydroxycarboxylic acid series, as with most of the direct cotton dyes,

(a) The presence of the acid amide group, —CONH— enhances substantivity (15–18). Further, it is known that *beta*-naphthol is considerably less substantive than the anilide of 3-hydroxy-2-naphthoic acid (4, 19), and that methylation of the —CONH— group to —CO—N— in the latter diminishes or destroys sub-

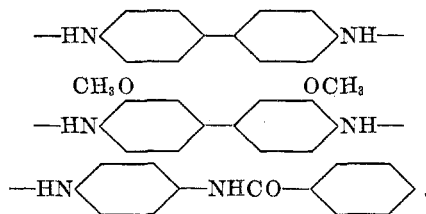


stantivity (3, 16);

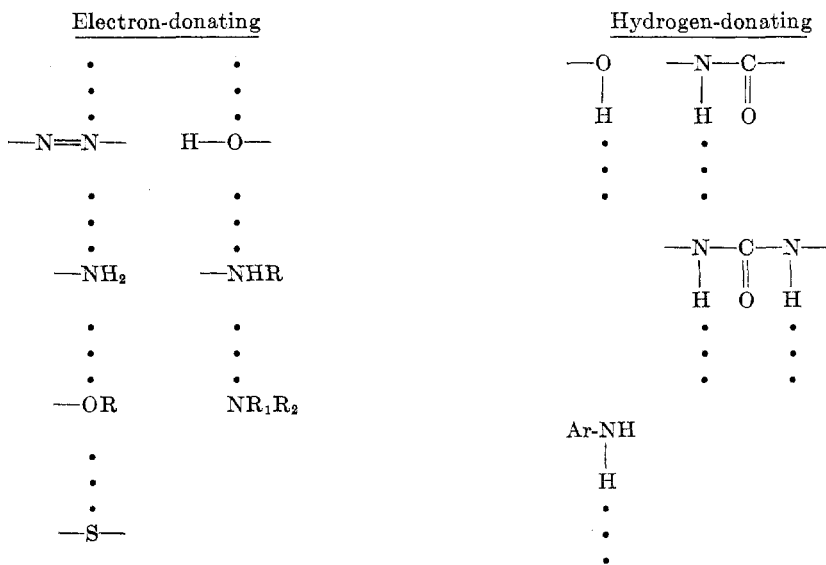
(b) Substantivity is affected or modified by the introduction of substituent groups into the arylamine radical (3) and generally speaking, (if the same acid is considered), the substantivity increases with the molecular weight (20). For example, anthracene derivatives are more substantive than analogous naphthalene products (1).

Increased cotton affinity is obtained from the introduction of known substantivity-conferring groups which are generally associated with the direct cotton dyes, namely:

1. The further extended conjugations ("bridges") (3) such as,



SUBSTANTIVITY-CONFERRING GROUPS



2. Groups which carry lone pairs of electrons, capable of acting as electron donors, and those which carry hydrogen atoms capable of co-ordinating, *i.e.* accepting, electrons from an external source (forming a hydrogen bond with another group) as shown on page 1293 (21).

However, not only the nature of the group, but the position of the substituent appears to display an important influence on substantivity (3, 22), and small changes in substituents may alter entirely the substantivity relations (19, 23-25).

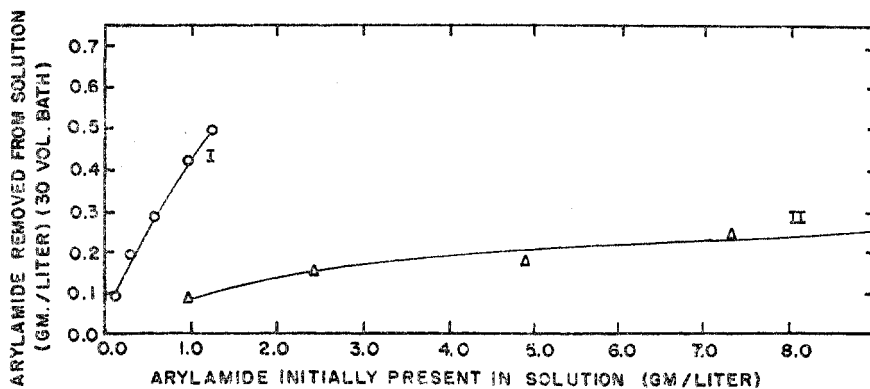
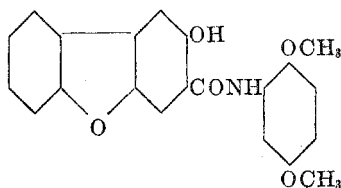


FIG. 1. EFFECT OF 30% ETHYL ALCOHOL ON SUBSTANTIVITY^a. Absorption of "Naphthol" AS-DB,

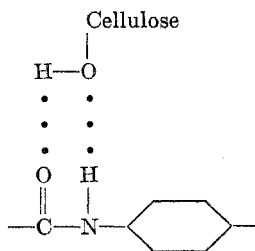


on cotton at 25-30° in (I) H₂O, NaOH; and (II) H₂O, C₂H₅OH, NaOH.

^a Substantivity calculated as % exhaustion $\left[\frac{y}{x}(100)\right]$, where y = arylamide removed and absorbed by cotton from solution (g./liter) and x = arylamide initially present in solution (g./liter).

HYDROGEN BOND THEORY (21, 26)

The above mentioned hydrogen bond linkage of cellulose with hydroxyl groups with direct dyes containing substantive amide groups has been visualized (27) as:



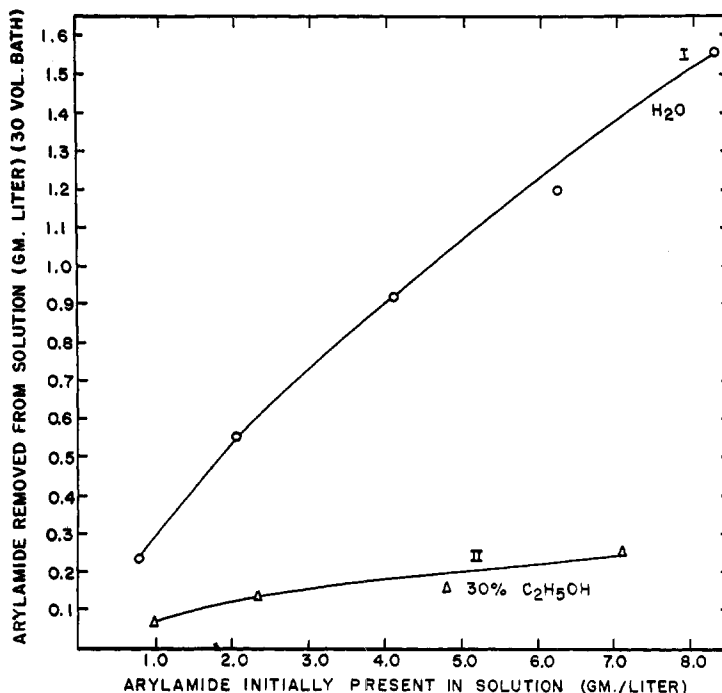
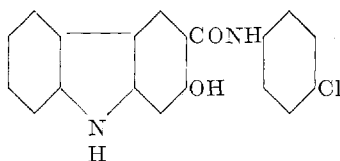
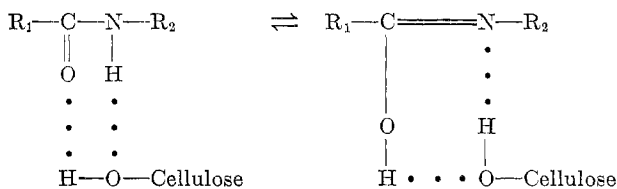


FIG. 2. EFFECT OF 30% ETHYL ALCOHOL ON SUBSTANTIVITY. Absorption of "Naphtol" AS-LB,



on cotton at 25-30° in (I) H₂O, NaOH; and (II) H₂O, C₂H₅OH, NaOH.

For the subject arylamides, hydrogen bonding of the possible amide forms with the hydroxyl groups of cellulose as follows, has been suggested (28).



This conception of cotton substantivity, which postulates that coordinated hydrogen furnishes the link between cellulose and direct cotton dyes, is in good agreement with experimental facts, as follows:

1. The hydroxyl groups of the cellulose appear to be involved in the bonding since esterification of the cellulose inhibits its capacity for absorbing direct dyes;

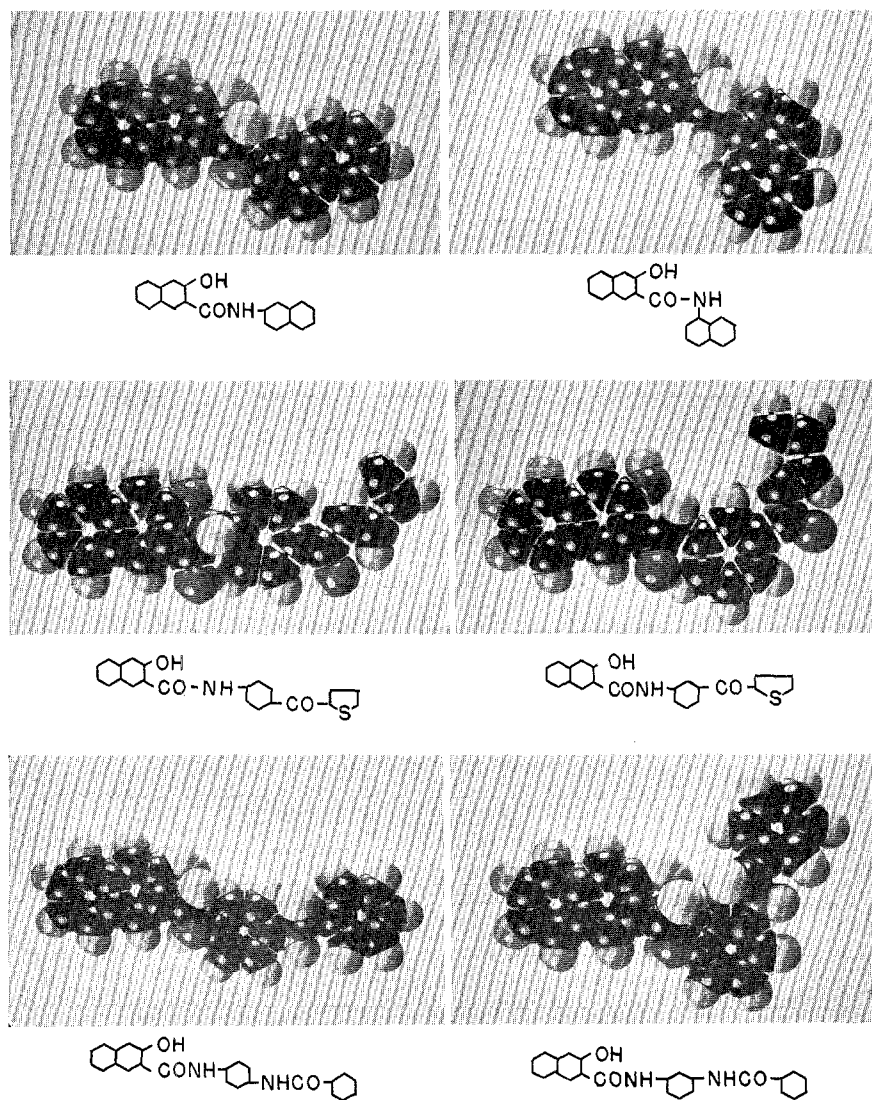


FIGURE 3

**SCALE MODELS OF ISOMERIC ARYLAMIDES SHOWING
LINEAR AND ANGULAR CONFIGURATIONS**

2. In a selected direct dye (29), the heat of dyeing (energy release) for each substantive group fixed has been shown to be about 7 kilocalories, which is the order of energy to be expected for hydrogen bond formation (30).

3. Scale models of substantive dyes have been found to fit well alongside of models of the cellulose chain. The substantive dye models display long chain-like structures, while nonsubstantive dyes have shorter, and less linear structures. Deviations from linear configuration in a dye molecule decrease its substantivity for cellulose. See planar diagram, p. 1298.

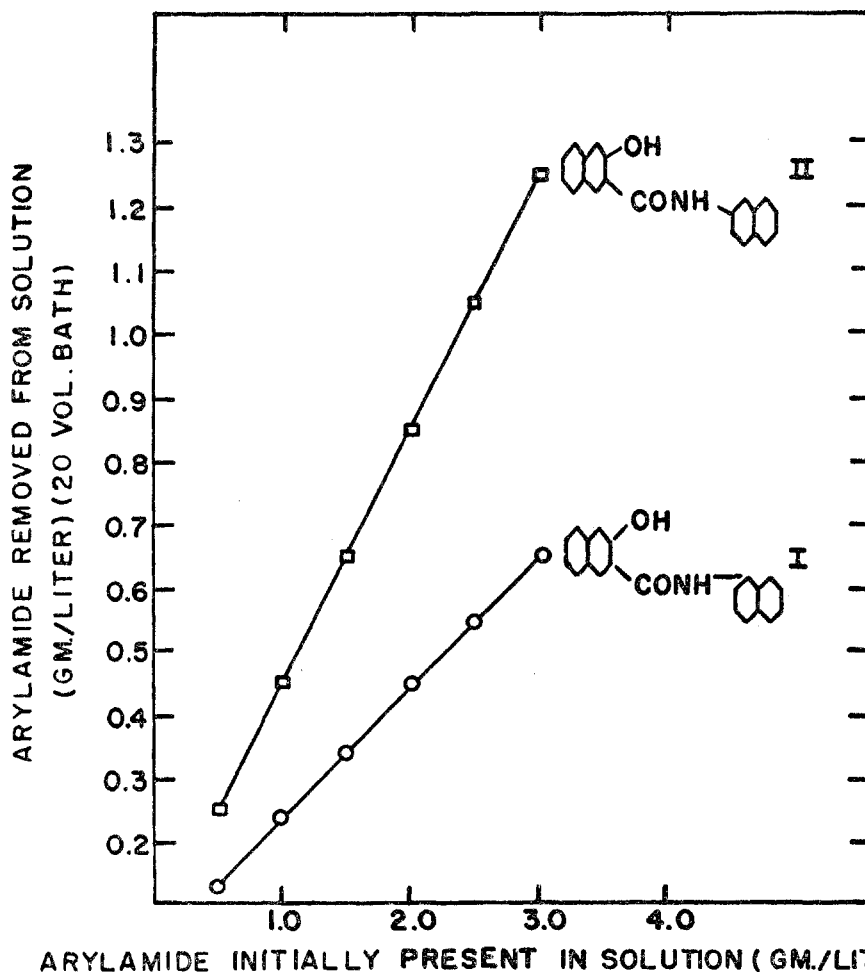
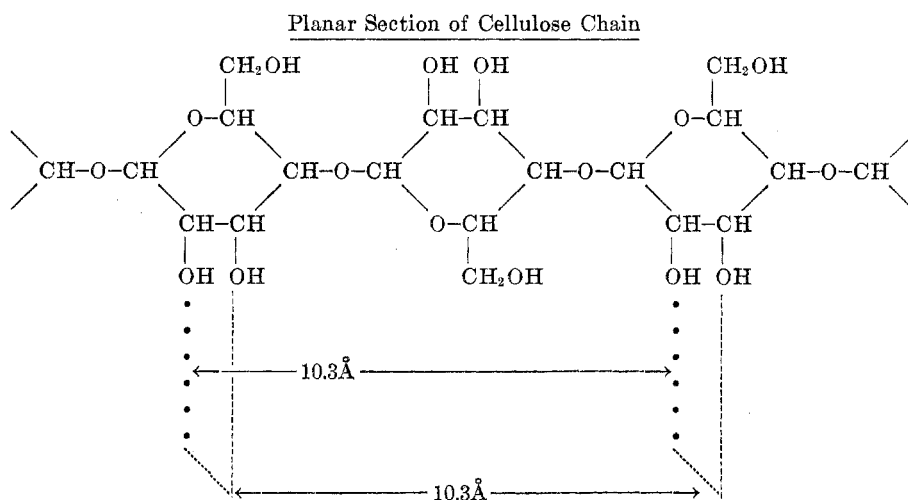


FIG. 4. EFFECTS OF LINEAR AND ANGULAR CONFIGURATIONS ON SUBSTANTIVITY. Absorption of (I) "Naphthol" AS-BO, and (II) "Naphthol" AS-SW on cotton at 25-30° (4). % Exhaustion: (I), 21-26; (II), 41-50.

4. It has been further observed that more stable fixations occur when the dye molecule not only forms, like cellulose, a straight linear chain, but when the aromatic nuclei are capable of assuming a coplanar arrangement, and when two or more substantive groups (or substantivating links) of the dye are situated alternately at a distance of 10.3 to 10.8Å units or multiples thereof, corresponding to the periodicity of the cellobiose units which make up the cellulose chain.

Our studies, described below, further exemplify the above relationship between substantivity and spacial arrangement, and extend the evidence advanced for cotton substantivity of azo colors to colorless "Naphthanil" coupling components.



EXPERIMENTAL

PREPARATION OF ARYLAMIDES

The arylamides, further discussed below, which were not commercially available and whose cotton substantivity had not been adequately recorded in the literature, were prepared by the generally known procedure of condensing amines, or their hydrochlorides with 3-hydroxy-2-naphthoic acid in inert solvents with dehydrating agents such as phosphorus trichloride, or phosphorus oxychloride (31). The *N*-(3-hydroxy-2-naphthoyl)-*N'*-benzoyl *m*-phenylenediamine [Figs. 3 (Bottom, right), 6] was obtained by catalytic hydrogenation of *N*-(3-hydroxy-2-naphthoyl)-*m*-nitroaniline (Naphthanil BS) to *N*-(3-hydroxy-2-naphthoyl)-*m*-phenylenediamine followed by condensation of the latter with benzoyl chloride.

The condensation products obtained were purified and freed from unreacted initial components by (a) solution in alcoholic caustic soda and reprecipitation with mineral acids, (b) extraction with mild alkalis such as sodium bicarbonate, and/or (c) recrystallization from organic solvents (32).

The 2- (3- and 4-) aminobenzoylthiophenes used for the preparation of the arylamides shown in Figs. 3 (Center), 5 were obtained by condensation of the corresponding nitrobenzoyl chlorides with thiophene in carbon disulfide (33, 34), and subsequent reduction of the 2- (3- and 4-) nitrobenzoylthiophenes in alcoholic solution to amines with iron and acetic acid.

N-Benzoyl-*p*-phenylenediamine, and *N-p*-anisoyl-*p*- and *m*-phenylenediamine for the arylamides shown in Figures 3, 6, and 7 were obtained in a similar manner, by reduction of condensation products from *m*- and *p*-nitroanilines with benzoyl and anisoyl chlorides (35-37).

Similarly *N*-monothenoyl-*p*-phenylenediamine for the arylamide shown in Fig. 19 was produced from thiophene-2-carbonyl chloride and *p*-nitroaniline (38).

The 4-aminobenzophenone employed for the arylamide in Fig. 17 was purchased from Dow Chemical Co.

Mesidine (39) (2,4,6-trimethylaniline), used for the preparation of the arylamide shown in Fig. 15, was obtained by catalytic hydrogenation with nickel in methanol from nitro-mesitylene which was purchased from the Eastman Kodak Co.

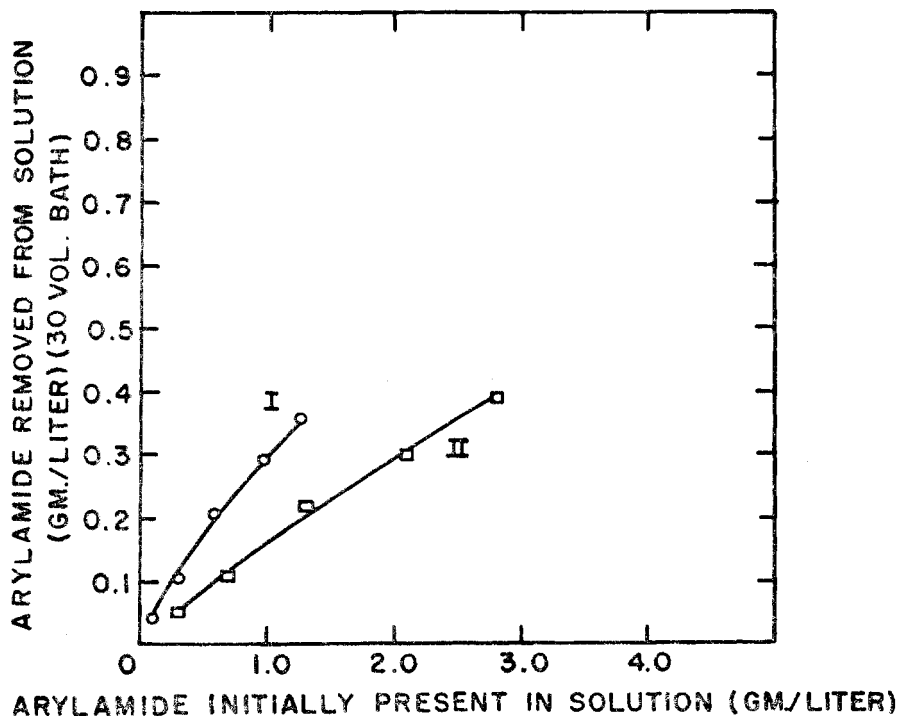
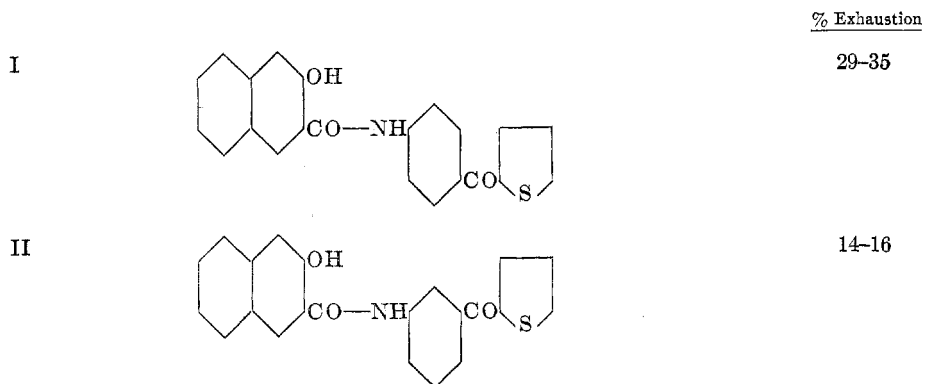


FIG. 5. EFFECTS OF LINEAR AND ANGULAR CONFIGURATIONS ON SUBSTANTIVITY. Absorption of (I) N-(3-hydroxy-2-naphthoyl)-2-(4-aminobenzoyl)thiophene and (II) N-(3-hydroxy-2-naphthoyl)-2-(3-aminobenzoyl)thiophene on cotton at 25-30°.



Purified pseudocumidine (40) (2,4,5-trimethylaniline) was separated from crude material purchased from the National Aniline Co. by fractional distillation and subsequent crystallization of distilled fractions.

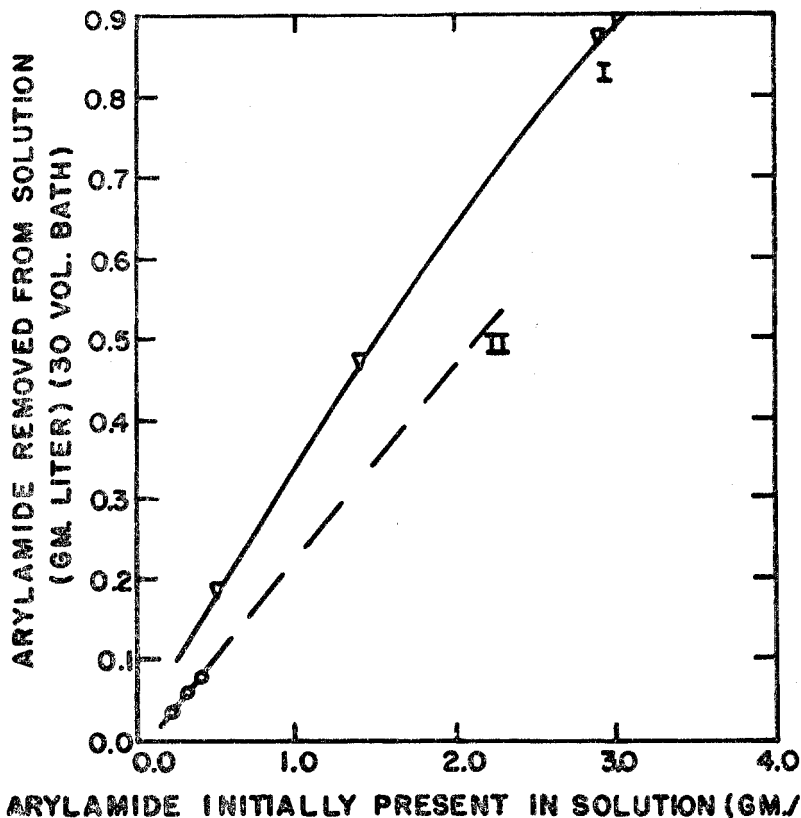
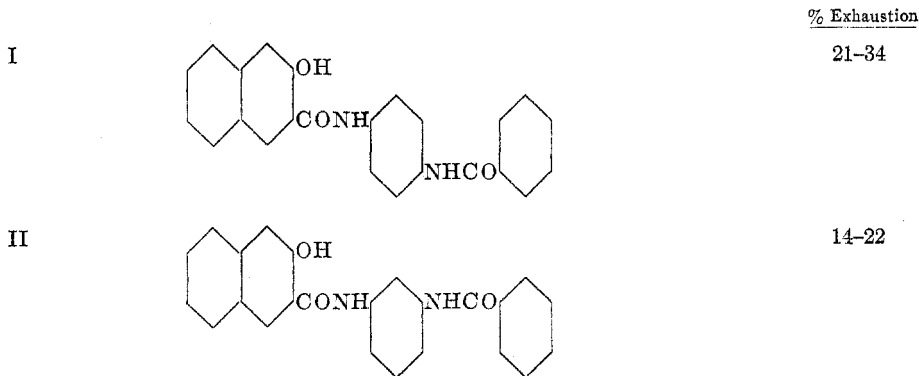


FIG. 6. EFFECTS OF LINEAR AND ANGULAR CONFIGURATIONS ON SUBSTANTIVITY. Absorption of (I) N-(3-hydroxy-2-naphthoyl)-N'-benzoyl-*p*-phenylenediamine and (II) N-(3-hydroxy-2-naphthoyl)-N'-benzoyl-*m*-phenylenediamine on cotton at 25-30°.



2,6-Dimethoxyaniline (41) was prepared from 2-aminoresorcinol (purchased from the Eastman Kodak Co.) by methylation with dimethyl sulfate in acetic anhydride and subsequent deacetylation of the dimethoxyacetanilide.

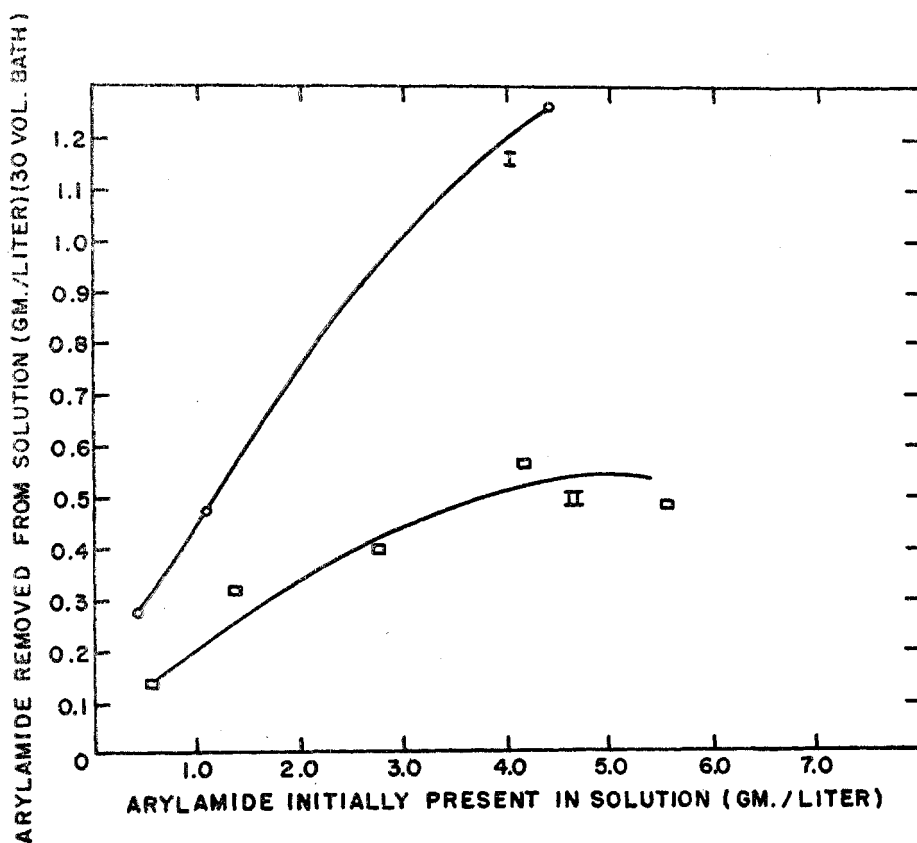
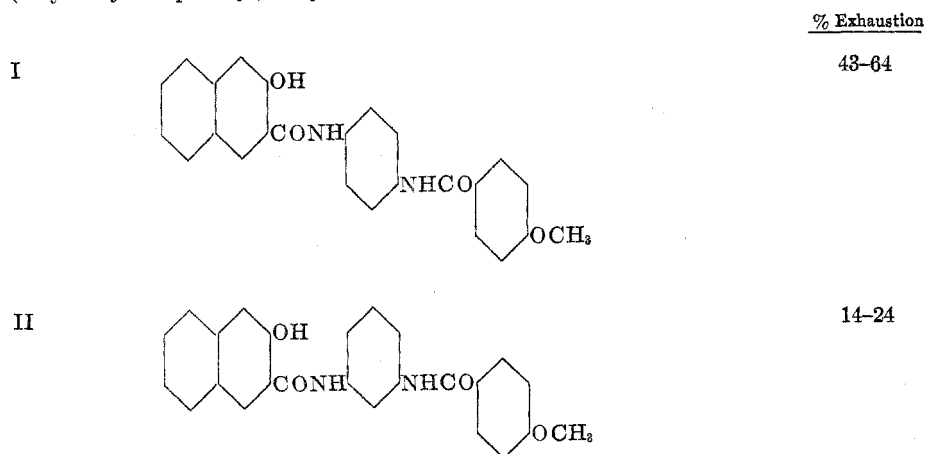


FIG. 7. EFFECTS OF LINEAR AND ANGULAR CONFIGURATIONS ON SUBSTANTIVITY. Absorption of (I) *N*-(3-hydroxy-2-naphthoyl)-*N'*-*p*-anisoyl-*p*-phenylenediamine and (II) *N*-(3-hydroxy-2-naphthoyl)-*N'*-*p*-anisoyl-*m*-phenylenediamine on cotton at 25-30°.



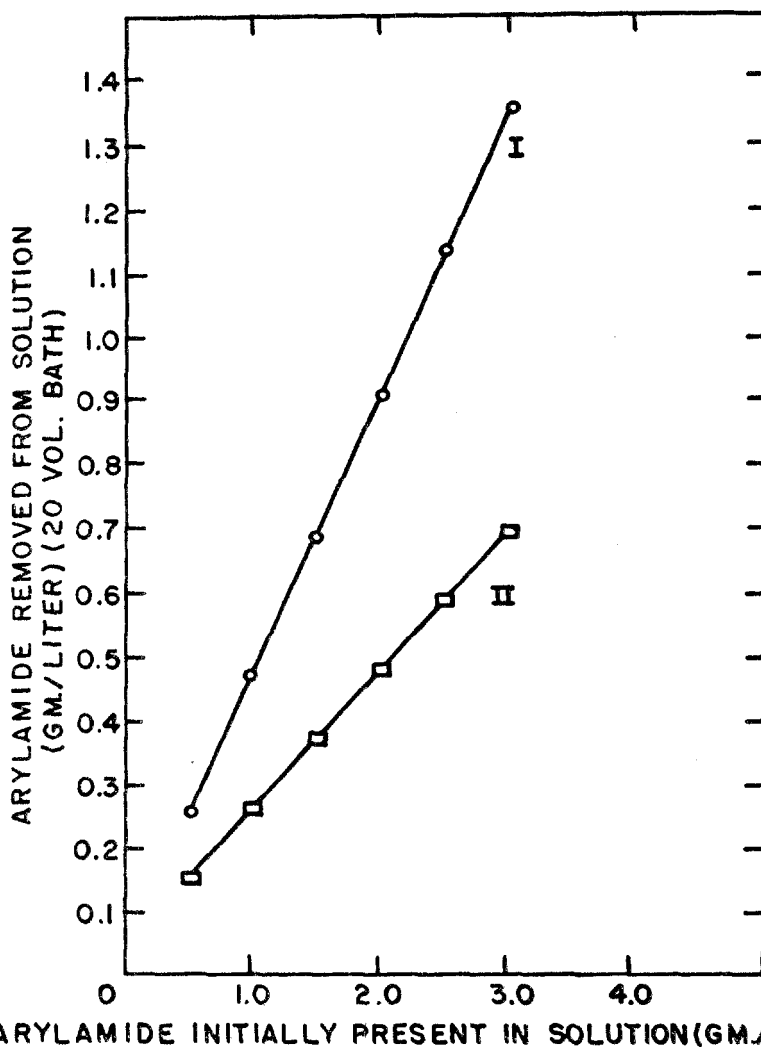
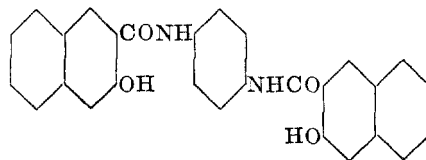


FIG. 8. EFFECTS OF LINEAR AND ANGULAR CONFIGURATIONS ON SUBSTANTIVITY. Absorption of (I) Di-(3-hydroxy-2-naphthoyl)-*p*-phenylenediamine and (II) Di-(3-hydroxy-2-naphthoyl)-*m*-toluylenediamine on cotton at 25-30° (4).

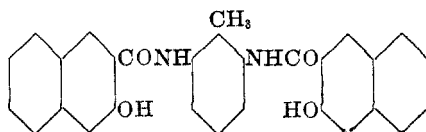
I



% Exhaustion

45-47

II



23-26

SUBSTANTIVITY VALUES

In Figures 4, 8, 10, 13, and 18 are plotted absorption values of a number of arylamides on cotton at 25-30°, where the yarn-to-liquor ratio was 1:20, which have been reported by Scheel (4). Other arylamide values shown where the ratio of yarn-to-liquor was 1:30, were obtained by a modification of the gravimetric method described by Bhat, *et al.* (1) and

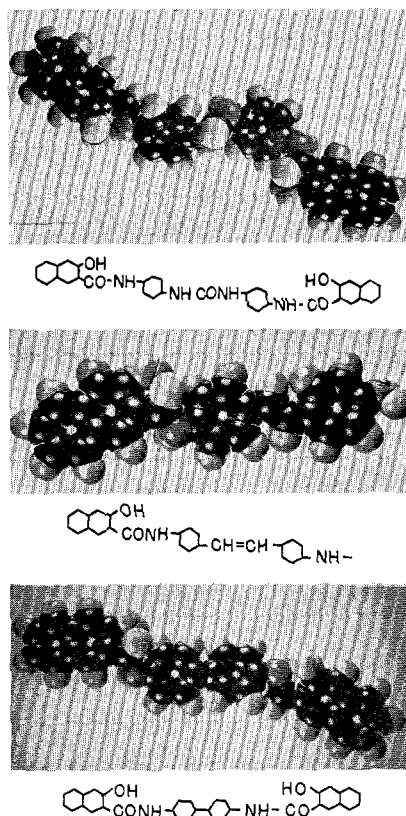
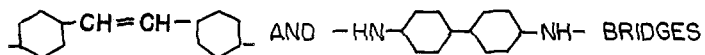


FIGURE 9

SCALE MODELS SHOWING SLIGHTLY ANNULAR CONFIGURATION FROM
-NH-CO-NH- BRIDGE, AND MORE LINEAR CONFIGURATION FROM



Moualim (42). No ethyl alcohol, however, was used to increase the solubility of the arylamide, since as observed by Bhat, and further illustrated in Figures 1 and 2, the presence of alcohol in the alkaline arylamide solution decreases the cotton affinity of the arylamide considerably.

The arylamide (2 g.) under examination was pasted with 30 ml. of distilled water containing 1.6 g. of caustic soda, then diluted with 170 ml. of water and warmed to 50° to effect solution. After cooling to 25-30°, the mixture was clarified by filtration through a Filter-

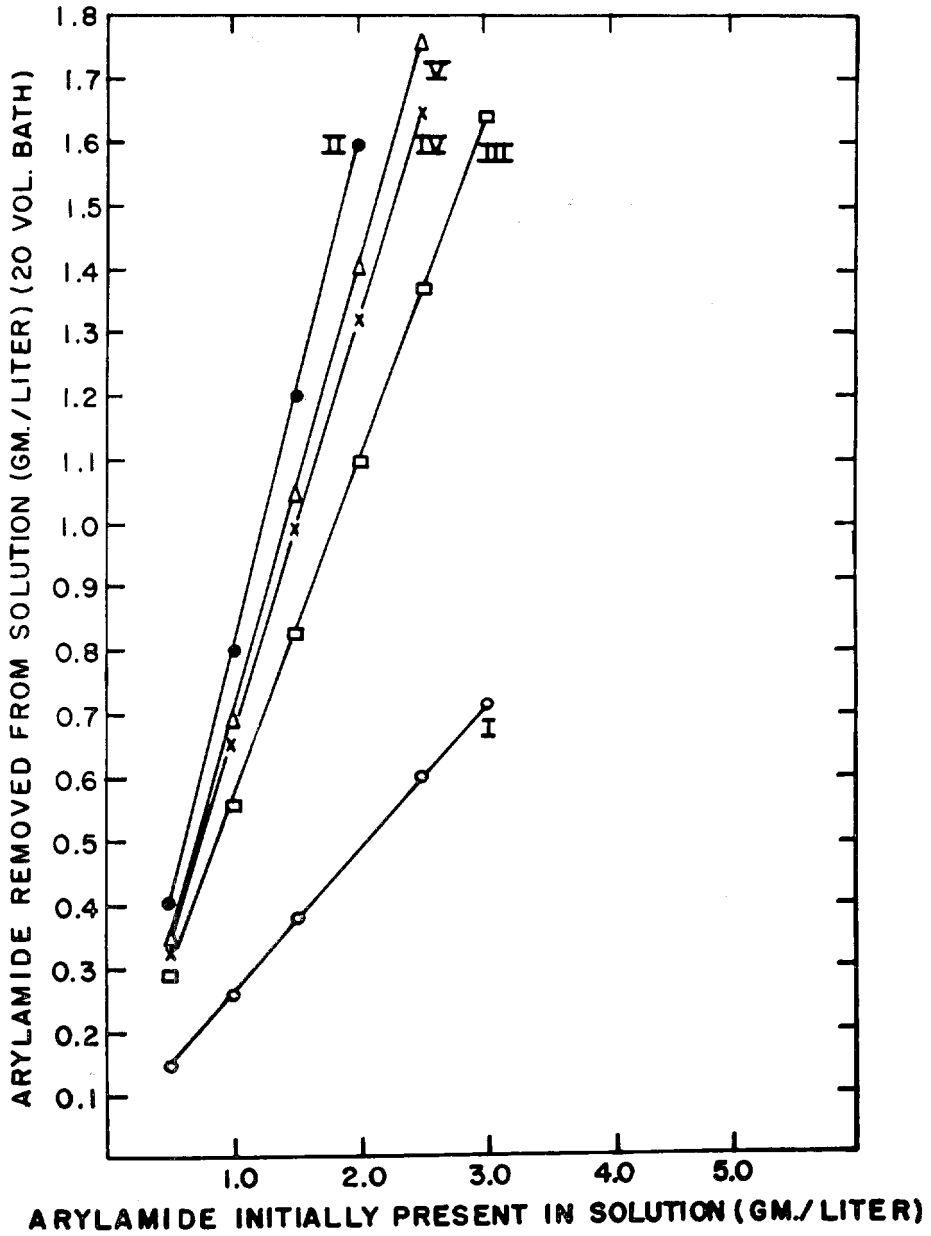


FIG. 10

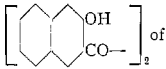
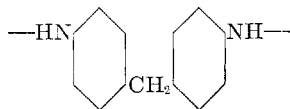
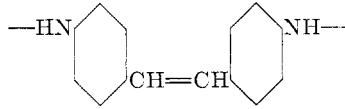

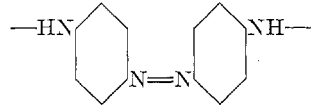
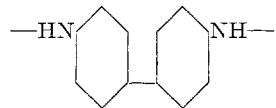
Cel mat, and the clear filtrate was diluted to 200-ml. volume with water. From this solution, other solutions of approximately 0.1, 0.25, 0.50, 0.75, and 1% concentrations were prepared by pipetting 4.5, 11.25, 22.5, 33.75, and 45 ml. of the filtrate followed by dilution of these

portions with water to 45 ml. total volume. Cotton yarn skeins,² each weighing 1.500 g. were then impregnated at the various concentrations for 30 minutes, while stirring at 5-minute intervals to assure complete saturation. The skeins were then removed, while squeezing excess liquor from them with a glass rod. Then 25-ml. samples of the residual solution were diluted to 175 ml. with water, and the residual arylamide assayed by precipitation with excess concentrated hydrochloric acid. The precipitated arylamide was collected on a tared Gooch crucible, washed with water, and dried at 100° to constant weight. The initial concentration of the arylamide solutions before treatment with the cotton skeins was also determined by precipitation with acid. The arylamide absorbed (expressed in g./liter) was then calculated by difference.

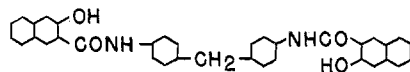
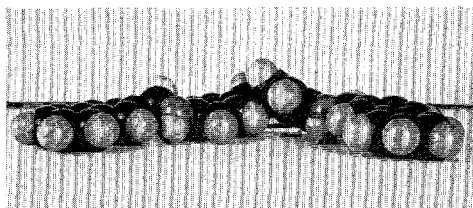
USE OF SCALE MODELS

Scale models of the arylamides were constructed from Fisher-Taylor-Hirschfelder Atom Models. Based on electron diffraction studies, the linear scale of one cm. in the model is

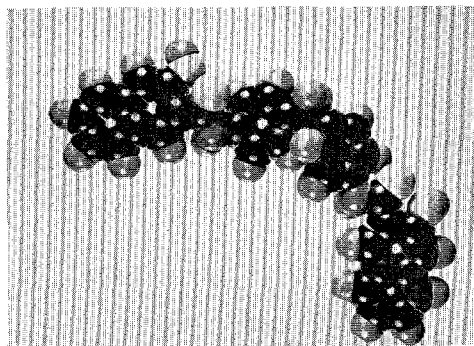
FIG. 10. EFFECTS OF LINEAR AND ANGULAR CONFIGURATIONS AND NON-COPLANAR EFFECT OF A $-\text{CH}_2-$ BRIDGE ON SUBSTANTIVITY. Absorption of di-(3-hydroxy-2-naphthoyl) derivatives of (I) 4,4'-diaminodiphenylmethane, (II) 4,4'-diaminostilbene, (III) 4,4'-diaminodiphenyl urea, (IV) 4,4'-diaminoazobenzene, and (V) benzidine on cotton at 25-30° (4).

	 of 2	
I		24
II		80
III		55
IV		66
V		70

² Bleached cotton yarn, boiled in Turkey Red Oil (5 g./liter), washed thoroughly with water, and dried at 105°.



(SIDE VIEW)



(TOP VIEW)

FIGURE 11

SCALE MODEL OF DI[2:3 HYDROXYNAPHTHOYL]
4 4' DIAMINO DIPHENYL METHANE SHOWING
ANGULAR CONFIGURATION AND NON-COPLANAR EFFECT
OF -CH₂ - BRIDGE

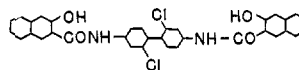
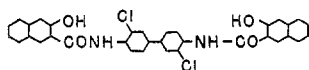
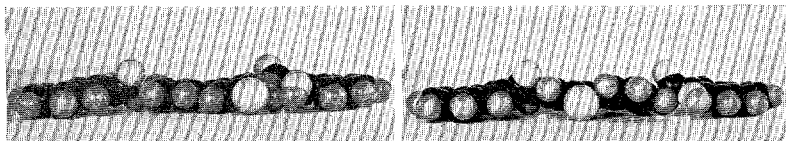


FIGURE 12

SCALE MODELS OF DI(2:3 HYDROXYNAPHTHOYL) DERIVATIVES OF
(LEFT) ORTHODICHLOROBENZIDINE, AND (RIGHT) m-DICHLOROBENZIDINE

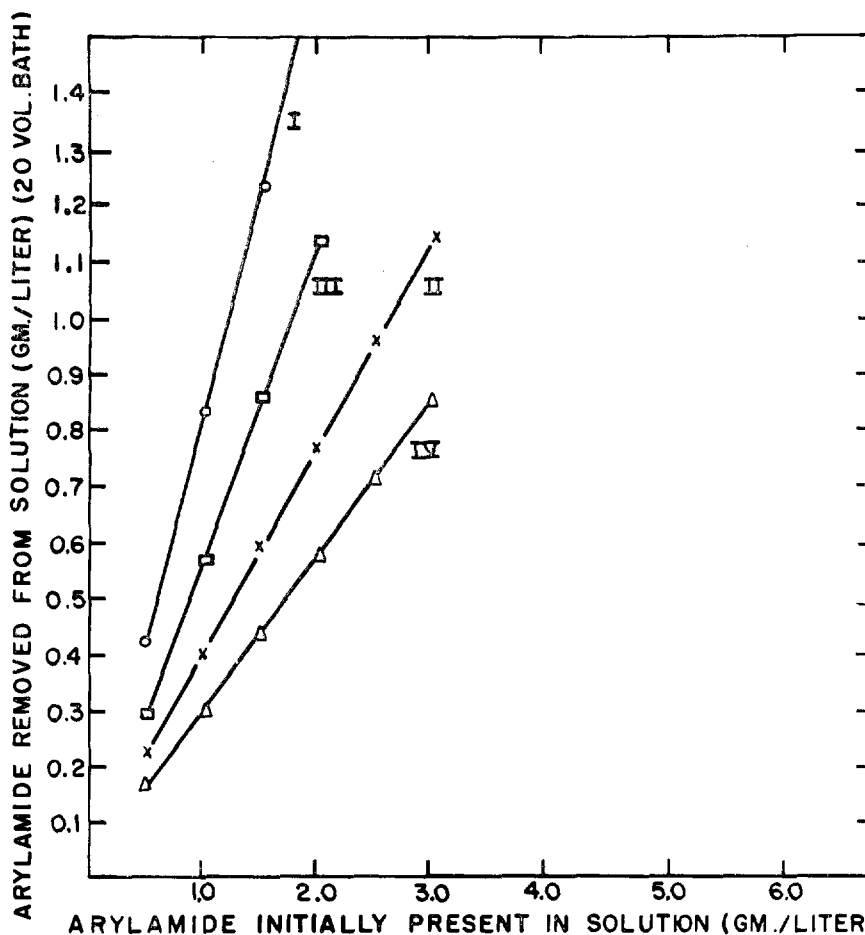


FIG. 13. COPLANAR CONFIGURATIONS: EFFECTS OF SUBSTITUTIONS WHICH DISTORT COPLANARITY. Absorption of di-(3-hydroxy-2-naphthoyl) derivatives of (I) *o*-dichlorobenzidine, (II) *m*-dichlorobenzidine, (III) *o*-tolidine, and (IV) *m*-tolidine on cotton at 25-30°(4).

	$\left[\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_3 \\ \\ \text{CO-} \end{array} \right]_2$ of	% Exhaustion
I		82
II		38
III		57
IV		29

equal to one Angstrom unit in the natural atom (43). It was then easy to examine in detail the spacial characteristics of the subject compounds, *i.e.*, linearity, planarity, distances between substantive groups, etc., and to determine how readily the models would fit alongside a model of the cellulose chain, and to relate these configurations with observed substantivity values.

Scale models of isomeric pairs of 3-hydroxy-2-naphthoylamides of (a) *alpha*- and *beta*-naphthylamines, (b) 2- (3- and 4-) aminobenzoylthiophenes, and (c) *N*-benzoyl-*m*- and *p*-

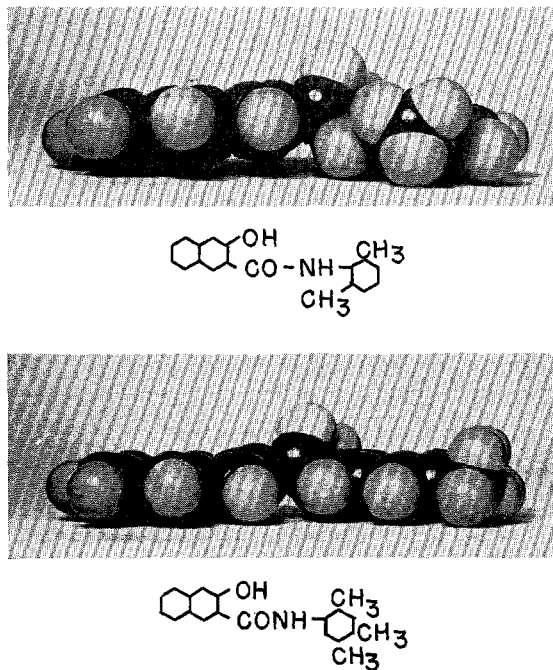


FIGURE 14

SCALE MODELS SHOWING EFFECT OF DI-ORTHO
SUBSTITUTIONS TO -CONH- GROUP UPON
COPLANAR CONFIGURATIONS

phenylenediamines are illustrated in Figure 3. The marked difference in configuration between isomers is readily apparent, *i.e.*, the *beta*-naphthamide is more linear than the *alpha* isomer; the 4-aminobenzoylthiophene derivative more linear than the 3-amino isomer; and the benzoyl-*p*-phenylenediamine derivative is linear, while the benzoyl-*m*-phenylenediamine derivative is definitely angular in shape.

Figures 4 to 8 inclusive, showing the absorption of isomeric pairs of the subject arylamides on cotton, establish the relationship between a straight linear structure and cotton

substantivity. Arylamides with linear configurations are considerably more substantive than isomers which are angular.

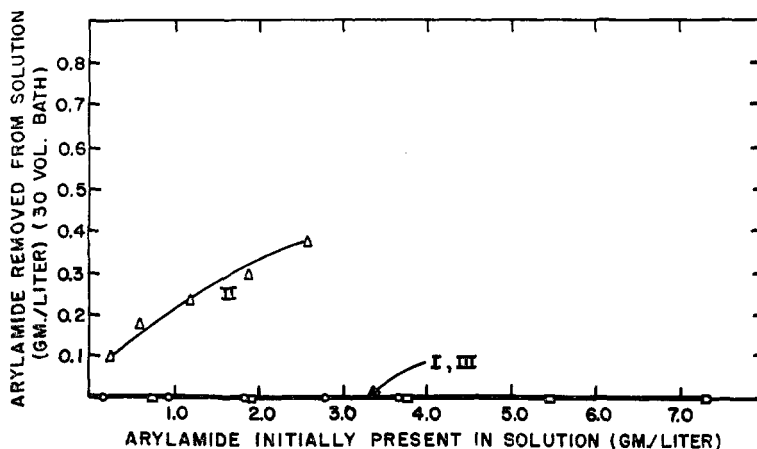


FIG. 15. EFFECTS OF SUBSTITUTION Di-ortho TO $-\text{CONH}-$ GROUP ON SUBSTANTIVITY. Absorption of 3-hydroxy-2-naphthoyl derivatives of (I) mesidine, (II) pseudocumidene, and (III) 2,6-dimethoxyaniline on cotton at 25-30°.

		% Exhaustion
I		0
II		20-28
III		0

In Figure 9, scale models of di-(3-hydroxy-2-naphthoyl) derivatives of (a) 4,4'-diaminodiphenyl urea, (b) 4,4'-diaminostilbene, and (c) benzidine are illustrated. The slightly angular configuration from the urea bridge, $-\text{NH}-\text{CO}-\text{NH}-$, and the more linear configurations from the stilbene, $-\text{CH}=\text{CH}-$, and the diphenyl, $-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-$, bridges are readily apparent. In Figure 10, the cotton ab-

sorption of these arylamides is shown. As might be expected (from their known effects in azo dyes), the two latter more linear configurations (Plots II and V) display noticeably greater exhaustion characteristics than the more angular urea configuration (Plot III).

A model of di-(3-hydroxy-2-naphthoyl)-4,4'-diaminodiphenylmethane is shown in Figure 11, which demonstrates the angular configuration, and the non-coplanar effect resulting from a methane, $-\text{CH}_2-$, bridge. It is known in azo colors that deviation from the straight linear structure of benzidine derivatives, as in colors derived from *p*-diaminodiphenylmethane, results in a reduction in cotton substantivity. This is again apparent in the arylamide series as is illustrated in Figure 10 (Plot I).

The effects of various substitutions or modifications which distort coplanar configurations and affect substantivity are further illustrated as follows: (Figures 12-17).

1. Figure 12 shows models of di-(3-hydroxy-2-naphthoyl) derivatives of (a) *o*-dichlorobenzidine and (b) *m*-dichlorobenzidine. The two chloro groups, when present *ortho* to the

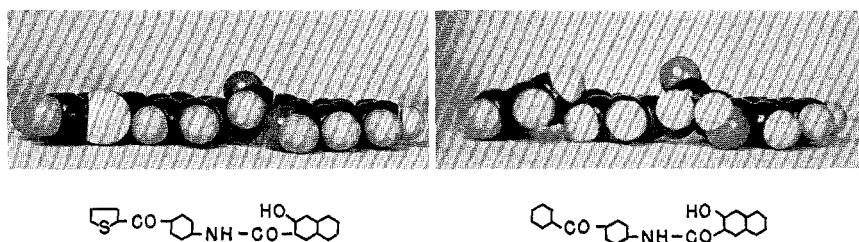
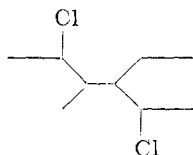


FIGURE 16

SCALE MODELS FOR (LEFT) N-2:3 HYDROXYNAPHTHOYL-2-(4 AMINO BENZOYL) THIOPHENE
AND (RIGHT) N-2:3 HYDROXYNAPHTHOYL-4- AMINOBENZOPHENONE

diphenyl linkage distort the coplanar configuration of the molecule. Such substitutions, as demonstrated in Figure 13, result in products with reduced substantivity.



2. The effects of di-*ortho* substitutions to the carbonamide, $-\text{CO}-\text{NH}-$, group are shown in Figures 14 and 15. The 2,6-dimethyl- and 2,6-dimethoxy- anilides display no affinity for cotton (zero substantivity). The scale models show that these amide molecules are not flat, *i.e.*, the configurations are not coplanar.

However, a polymethyl substituted anilide in which one of the *ortho* positions is left open, as in the 2,4,5-trimethyl anilide, is found to be substantive, and its scale model shows a coplanar configuration.

3. Scale models and absorption values for (a) N-(3-hydroxy-2-naphthoyl)-2-(4-amino-benzoyl)thiophene, and (b) N-(3-hydroxy-2-naphthoyl)-4-aminobenzophenone are shown in Figures 16 and 17. The benzoylthiophene derivative is more substantive and the molecule is flatter than the benzophenone derivative.

The absorption on cotton for a number of arylamides which are predominately linear and

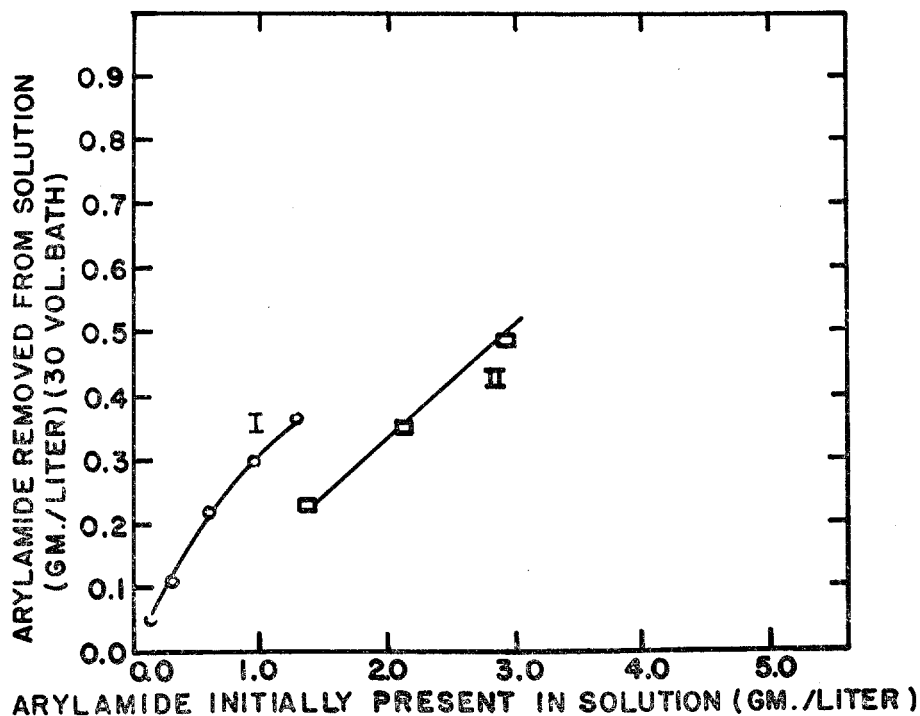
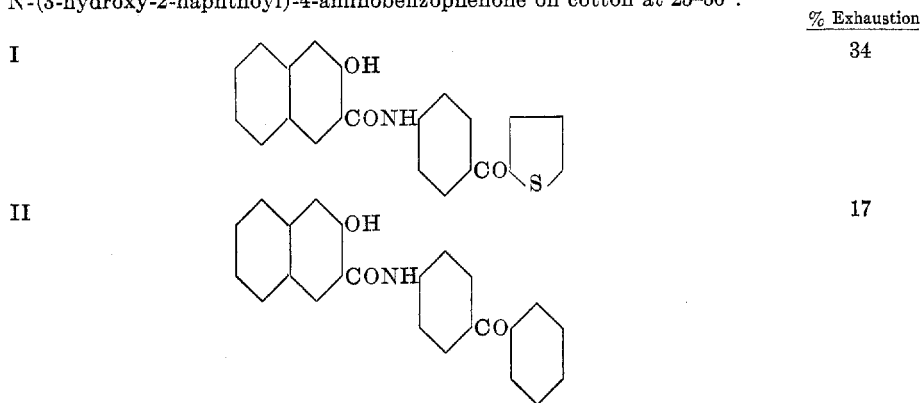
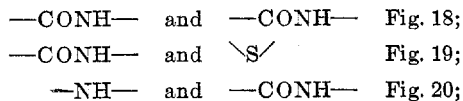


FIG. 17. EFFECTS OF COPLANAR AND NON-COPLANAR CONFIGURATIONS ON SUBSTANTIVITY. Absorption of (I) N-(3-hydroxy-2-naphthoyl)-2-(4-aminobenzoyl)thiophene and (II) N-(3-hydroxy-2-naphthoyl)-4-aminobenzophenone on cotton at 25-30°.



coplanar in configuration, and which contain a plurality of substantivity-conferring groups are shown in Figures 18 to 20. For the pairs of substantive links examined:



maximum cotton fixation is observed when these groups are situated 10Å units apart.

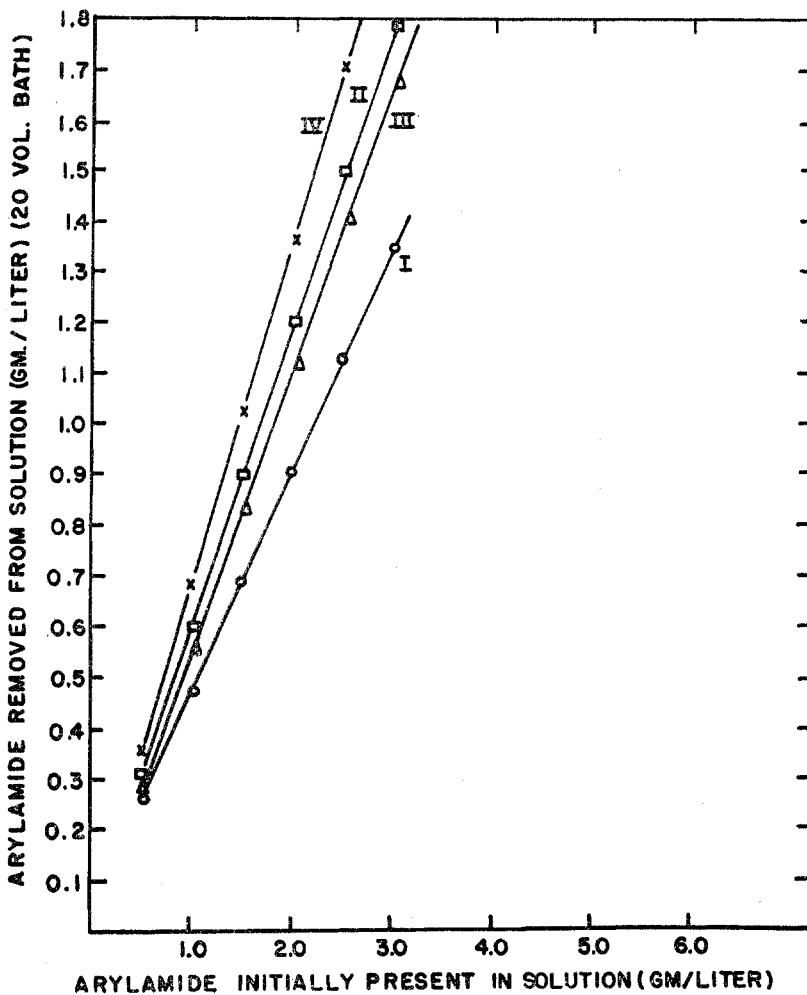


FIG. 18. EFFECTS OF INTERATOMIC DISTANCES BETWEEN PAIRS OF SUBSTANTIVE GROUPS. Absorption of di-(3-hydroxy-2-naphthoyl) derivatives of (I) *p*-phenylenediamine, (II) 1,5-naphthalenediamine, (III) 2,6-naphthalenediamine, and (IV) 1,6-naphthalenediamine on cotton at 25-30° (4).

		FROM SCALE MODELS	
		% Exhaustion	Interatomic distances between
			-CONH- and -CONH-
			← Å →
I		45	7.5
II		60	10.0
III		56	11.0
IV		68	10.0

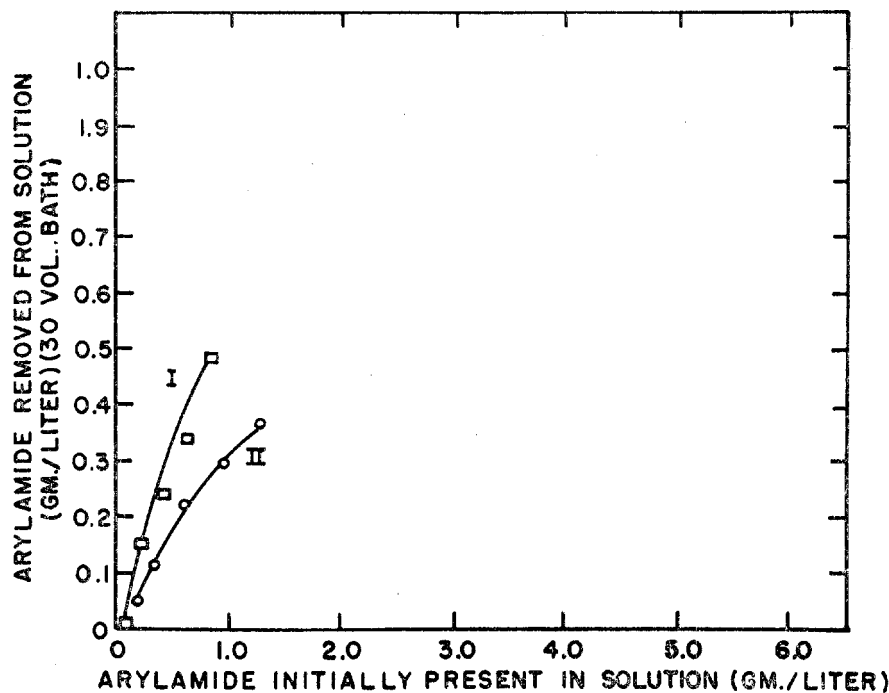

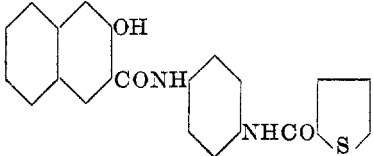
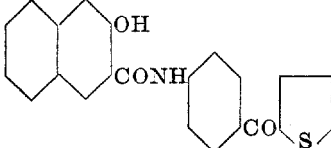


FIG. 19. EFFECTS OF INTERATOMIC DISTANCES BETWEEN PAIRS OF SUBSTANTIVE GROUPS. Absorption of (I) N-(3-hydroxy-2-naphthoyl)-N'-monothienoyl-*p*-phenylenediamine and (II) N-(3-hydroxy-2-naphthoyl)-2-(4-aminobenzoyl)thiophene on cotton at 25-30°.

		Interatomic distance between -CONH- and 	
		% Exhaustion	$ \leftarrow \text{Å} \rightarrow $
I		65	10.3
II		34	7.0

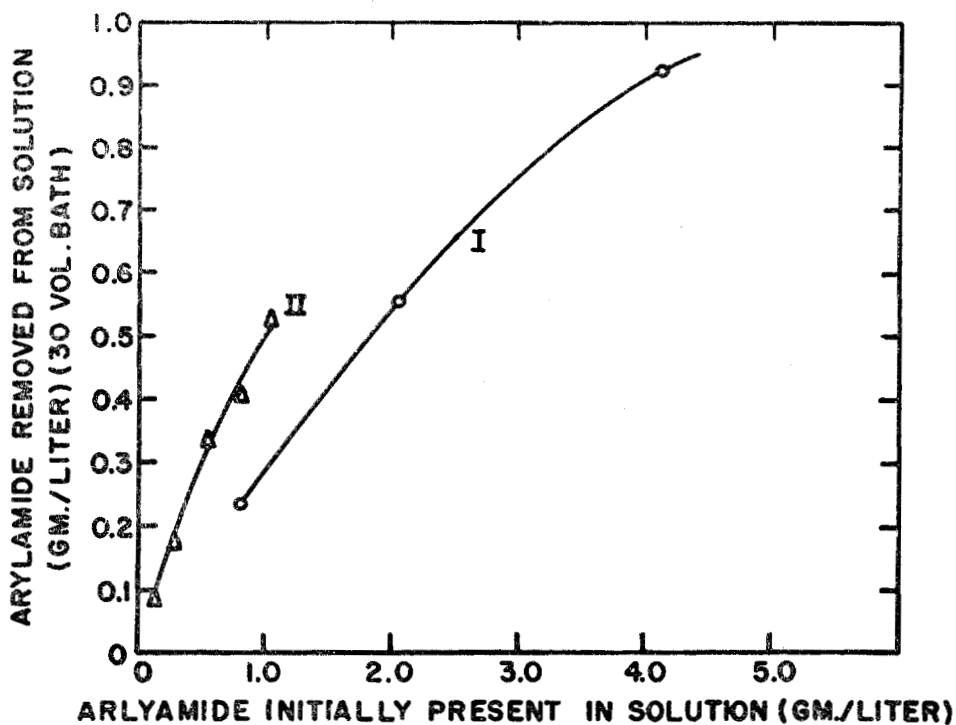
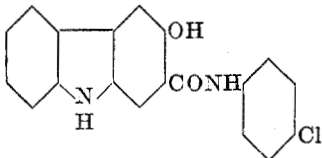
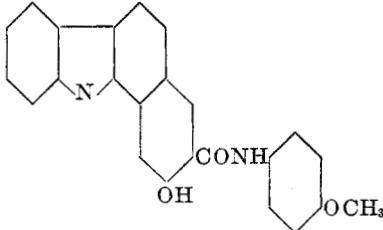
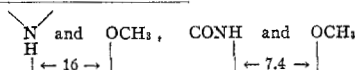


FIG. 20. EFFECTS OF INTERATOMIC DISTANCES BETWEEN PAIRS OF SUBSTANTIVE GROUPS. Absorption of (I) "Naphthol" AS-LB and (II) "Naphthol" AS-SG (Brenthol GB) on cotton at 25-30°.

	% Exhaustion	Interatomic distance between
		$\begin{array}{c} \diagup \text{N} \diagdown \\ \text{H} \\ \end{array}$ and $\begin{array}{c} -\text{CONH}- \\ \end{array}$ $\leftarrow \text{Å} \rightarrow$
I 	22-28	7.3
II 	62-70	10.0 ^a

^a Interatomic distances (Å)



Acknowledgements. The author expresses appreciation to D. E. Kvalnes for his invaluable suggestions and contributions, and thanks to C. E. Sparks, L. E. Schniepp, J. H. Trepagnier, M. E. Friedrich, C. W. Croco, and V. Weinmayr, members of the Jackson Laboratory Research Staff, for their assistance in the synthesis of some of the arylamides used in this investigation.

SUMMARY

Measurements from scale models of "Naphthanil" Coupling Components, and their substantivity values exemplify relationships between substantivity and spacial arrangement as follows:

(a) Products with linear configuration are more substantive than angular types.

(b) Products which are flat, or coplanar have better affinity for cotton than analogous or isomeric products which are non-coplanar.

(c) Substitutions or modifications which disrupt or disturb the coplanar configuration of the parent nucleus result in a reduction of substantivity.

(d) Maximum fixation to cotton occurs in compounds which are predominately linear and coplanar in configuration, and which contain a plurality of substantive groups, which are situated 10Å units, or multiples thereof, apart corresponding to the periodicity of the cellulose units which make up the cellulose chain.

These relationships are similar to those observed for direct cotton dyes and are in agreement with the conception that coordinated hydrogen furnishes the link between cellulose and the direct dye or the coupling component.

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