Studies on the Diacylaminoanthraquinone Dyes

By Takayuki HAYASHI and Reiko SHIBATA

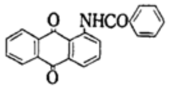
(Received September 20, 1960)

In our previous papers[1-5], 1-acylamino-, 1,4-, 1,5- and 1,8-diacylaminoanthraquinones having NO_2, Cl, OMe, $SO_2N(Me)_2$ or NH_2 (X or Y)* as a substituent in the acyl group were prepared. Visible and infrared absorption spectra of these dyes were measured in solution and in solid, respectively, and cotton was dyed with them, and their light fastness on cotton was tested. On the basis of these results, the effects of X and Y substituent groups were discussed with their various properties, such as wavelengths of absorption maxima, relative difficulties of vatting, color tones of vat solutions, shades of dyed cotton, and light fastness. In this paper, the abovementioned properties have been discussed correlatively for all of these dyes.

Results and Discussion

Visible Absorption Spectra.—Visible absorption spectra of 1-acylamino-, 1,4- and 1,5-diacylaminoanthraquinone series were observed and discussed by Peters and Sumner[6]. In this paper, from the results of visible absorption for 1-acylamino-, 1,4-, 1,5- and 1,8-diacylaminoanthraquinones, the relation between wavelengths or intensities of the absorption maximum and positions of acyl groups has been discussed. Furthermore, for each series of 1-acylamino-, 1,4-, 1,5- and 1,8-diacylaminoanthraquinones the effect of the substituent (X or Y) in the acyl group upon the wavelength and intensity of the absorption maximum has been considered.

The absorption maxima[1-4] of 1-benzoylamino-, 1,4-, 1,5- and 1,8-dibenzoylaminoanthraquinones appeared at 421, 502, 448 and 455 mμ in *o*-dichlorobenzene with the peak molar extinction coefficient of 5900, 7600, 12000 and 11000, respectively. Since the molecule of the 1,5-derivative is divided into two halves diagonally as in III, simple additivity is established between two chromophoric systems within it, and one to three benzene rings in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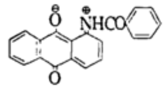
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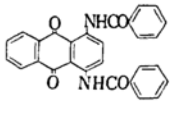
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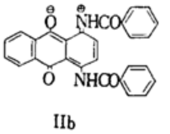
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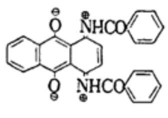
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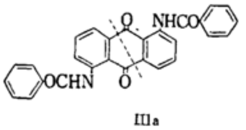
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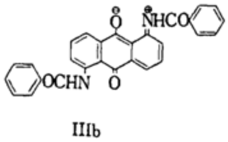
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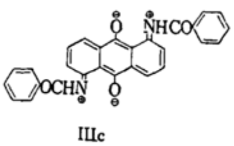
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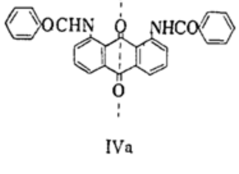
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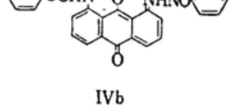
IVb

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1) T. Hayashi and R. Shibata, *J. Chem. Soc. Japan, Ind. Chem Sec.* (*Kogyo Kagaku Zasshi*), 63, 513 (1960).
2) T. Hayashi and R. Shibata, ibid., 63, 840 (1960).
3) T. Hayashi, ibid., 63, 1241 (1960).
4) T. Hayashi, ibid., 63, 1395 (1960).
5) T. Hayashi, ibid., 63, 1985 (1960).

* X or Y denotes a substituent in the acyl group of acylaminoanthraquinones.

6) R. H. Peters and H. H. Sumner, *J. Chem. Soc.*, 1953, 2101.

the anthraquinone nucleus increase their quinonoid character, thereby reducing the aromaticity, but the extent of the contribution of a structure IIIc to the resonance is exceedingly small. For the 1-derivative, on the other hand, one to two benzene rings in the anthraquinone nucleus increase their quinonoid character as in I, thereby reducing the aromaticity, and only one carbonyl group of the anthraquinone nucleus takes part in conjugation, this being different from the 1, 5-derivative. The wavelength of the absorption maximum for the 1, 5-derivative should therefore be somewhat longer than for the 1-derivative, but the intensity of the former should be approximately twice that of the latter. Since the molecule of the 1, 8-derivative is divided into two halves vertically as in IV, simple additivity is established between two chromophoric systems within it as the 1, 5-derivative, but one to two benzene rings in the anthraquinone nucleus increase their quinonoid character, thereby reducing the aromaticity, this being different from the 1, 5-derivative. Though one carbonyl group is held by two chromophoric systems in common for the 1, 8-derivative, mesomeric shifts of electrons within the chromophoric systems are suppressed, owing to cross conjugation of two systems, in which case the extent of the contribution of a structure IVb to the resonance should be a little greater than for a structure IIIb. The effective area of π-electron systems[7,8] for IV is also slightly smaller than for III. The wavelength of the absorption maximum for the 1, 8-derivative should therefore be somewhat longer than for the 1, 5-derivative, and the intensity of the former should be a little lower than for the latter but approximately twice that of the 1-derivative. For the 1, 4-derivative one to two benzene rings in the anthraquinone nucleus increase their quinonoid character, thereby reducing the aromaticity, and the extent of the contribution of a structure IIc to the resonance is more marked. The 1, 4-derivative shows no such simple additivity as indicated in III owing to interaction between their two chromophoric systems, probably producing a new one, and an effective area of π-electron systems for II is smaller than for III or IV. The wavelength of the absorption maximum for the 1, 4-derivative should therefore be the longest among them and the intensity should lie between those of 1- and 1, 8-derivatives. Such relations should be established similarly among 1-acylamino-, 1, 4-, 1, 5- and 1, 8-diacylaminoanthraquinones with the same substituent in the acyl group.

From results[1-4] of the bands for each series, it was known that electron-attracting substituents mainly showed a +I effect and electron-donating substituents mainly a −T effect and the *p*-dimethylsulfamyl group showed a +I effect similar to a *p*-nitro group, this being different from the result of the *p*-sulfamyl group obtained by Zollinger[9]. For the bands of each series, it was shown that the shifts of the absorption maximum complied with Hammett's rule[10] and that the relationship between the wavelengths of the absorption maximum and Brown's σ^+ values[11,12] was

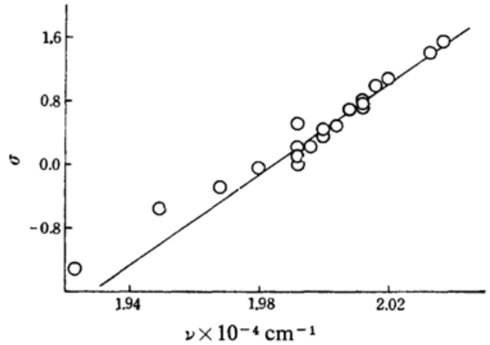

Fig. 1. The relationship between wave-number (ν) of the maximum absorption and Hammett's σ value on the 1, 4-diacylaminoanthraquinone series.

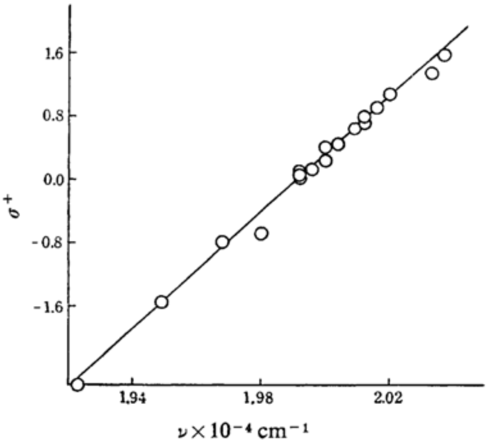

Fig. 2. The relationship between the wave-number (ν) of the maximum absorption and Brown's σ^+ value on the 1, 4-diacylaminoanthraquinone series.

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[7] E. A. Braude, ibid., **1950**, 379.

[8] R. H. Peters and H. H. Sumner, *J. Soc. Dyers Colorists*, **71**, 130 (1955).

[9] H. Zollinger and C. Wittwer, *Helv. Chim. Acta*, **39**, 347 (1956).

[10] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[11] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

[12] G. W. Gray, "Steric Effects in Conjugated Systems", Butterworths Scientific Publications, London (1958), p. **100**.

more linear than that between them and Hammett's σ values[10] as indicated in Figs. 1 and 2 for the 1, 4-diacylaminoanthraquinone series. Accordingly it is possible to estimate a shift from Brown's σ^+ value of a substituent in the acyl group and obtain an expected shift of the absorption maximum by introduction of an adequate substituent with known Brown's σ^+ value to the acyl group. Hammett's σ value of *p*- and *m*-dimethylsulfamyl groups were 0.70 and 0.53, and Brown's σ^+ values of these were 0.86 and 0.68, respectivery, from Figs. 1 and 2.

For each series, dyes with *o*-chloro, *o*-methoxy or *o*-nitro groups, besides an *o*-amino group, as X and Y, showed a considerably hypsochromic shift and a decreasing intensity in their absorption maxima. Both the wavelengths and the intensities were almost independent of all combinations of substituents in two acyl groups for each series. As indicated in Table I, the absorption maximum of 1, 5-diacetylaminoanthraquinone agreed with those of 1, 5-di-*o*-substitutes. This fact was admitted on the other *o*-substitutes. The effect of the *o*-substituted phenyl group should therefore be much the same as that of the methyl group, and this fact shows that the benzene ring has been twisted around the C–C linkage between the *o*-substituted phenyl and the carbonyl group in the acyl group. The twisting may be attributed to the steric hindrance between the *o*-nitro and the carbonyl group or to the repulsion between the *o*-chloro or *o*-methoxy and the carbonyl group in the acyl group. The wavelengths of the absorption maximum of 1-*o*-amino-, 1, 4-, 1, 5- and 1, 8-di-*o*-amino-substitutes were 436, 514, 460 and 463 mμ in *o*-dichlorobenzene, respectively. As these absorption peaks do not show a hypsochromic shift, they are different from the ones of the other *o*-substitutes, such the interesting twisting of the benzene ring as in *o*-substitutes may not arise.

TABLE I. VISIBLE ABSORPTION BANDS OF *o*-SUBSTITUTED BENZOYLAMINO- AND ACETYLAMINOANTHRAQUINONES[1–4]

	o-Substitute	Acetylamino-anthraquinone
1-Derivative	407～411 (5300～6000)**	415 (5300)
1, 4-Derivative	483～486 (6950～7100)	487 (7550)
1, 5-Derivative	437～439 (10500～11500)	438 (11000)
1, 8-Derivative	438～441 (9700～10200)	440 (10400)

Infrared Absorption Spectra.—Three and six μ bands of infrared absorption spectra for some acylaminoanthraquinones have been observed as powders suspended in Nujol on account of their limited solubility and were discussed by Flett[13]. In this work, infrared absorption spectra of 1-acylamino-, 1, 4-, 1, 5- and 1, 8-dibenzoylaminoanthraquinones have also been observed as powders suspended in Nujol and information has been gained about their structures in the solid. This information may be, to some extent, similar to deduction for the structure of the dye molecule in cotton dyed with them.

As indicated in Table II, a C=O frequency in the peri-position of the benzoyl group for 1, 4-dibenzoylaminoanthraquinone is lower than for the 1, 5-isomer, and then the C=O bond of the former is more weakened than for the latter. This fact may generally suggest that the shade of the 1, 4-diacylaminoanthraquinone series on cotton is more bathochromic than in the case of the 1, 5-isomer. As 3 μ bands of 1, 5-dibenzoylaminoanthraquinone almost agree with those of the 1, 8-isomer, the effect of imino groups on the whole of the molecule is much the same in both cases. This fact may generally suggest that a shade of the 1, 5-diacylaminoanthraquinone series on cotton is approximately the same with that of the 1, 8-isomer.

TABLE II. 3 AND 6 μ BANDS OF SOLID BENZOYLAMINOANTHRAQUINONES[5]

	3 μ bands cm^{-1}	6 μ bands cm^{-1} (C=O frequencies)
1-Derivative	3175	1681, 1669, 1637
1, 4-Derivative	3125, 3086, 3058	1686, 1639
1, 5-Derivative	3226, 3195, 3125[a]	1689, 1639
1, 8-Derivative	3226, 3185, 3125[a]	1701, 1681, 1631

a) 3 μ bands obtained from KBr discs of 1, 5- and 1, 8-derivatives were all the same (3257, 3226, 3125 cm^{-1}).

Though it is known that the question, whether or not shifts of a C=O frequency comply with Hammett's rule, must be generally discussed in regard to the result obtained from the dilute solution of a nonpolar solvent, the results obtained from the solid of the 1-acylaminoanthraquinone series have been examined on account of its limited solubility in the present work. Shifts in the C=O frequency of the acyl groups were in harmony with Hammett's rule, as indicated in Fig. 3. Shifts in the C=O frequency of the peri-position of the acyl groups lay on the S-shaped curve against

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** Wavelength, mμ (molar extinction coefficient).

[13] M. S. C. Flett, *J. Chem. Soc.*, **1948**, 1441.

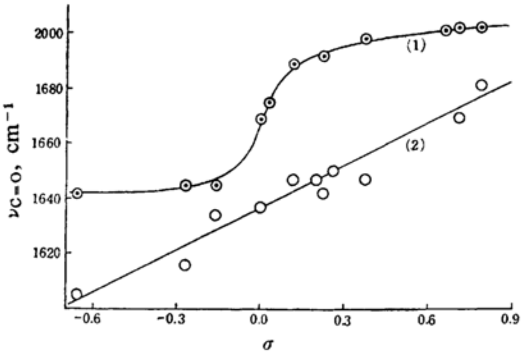

Fig. 3. The relationship between the C=O frequency ($\nu_{C=O}$) and Hammett's σ value on the 1-acylaminoanthraquinone series.
(1) The quinone-type C=O frequency in the peri-position of the acylamino group.
(2) The C=O frequency in the acyl group.

Hammett's σ value, as indicated in Fig. 3, and the latter C=O bond was therefore strengthened to much the same degree for the dyes with any of the electron-attracting substituents and the reverse was found to be true for the dyes with any of the electron-donating substituents. For the 1-derivative with a *p*- or *m*-dimethylsulfamyl group which is intensely electron-attracting, the C=O bonds of its molecule in solid have been strengthened to the extent indicated on the curve of Fig. 3.

As C=O frequencies[5] of (*o*-nitrobenzoyl)-aminoanthraquinone agree with those of 1-acetylaminoanthraquinone[13], the effect of the *o*-nitrophenyl group on them is thought to be of the same degree as that of the methyl group. This fact shows that the benzene ring of the former has been twisted around the C–C linkage between the *o*-substituted phenyl and the carbonyl group in the acyl group, and that the twisting may be attributed to steric hindrance between the *o*-nitro and the carbonyl group in the acyl group. For the *o*-nitro-substitute, this interpretation of its molecular structure in solid is the same as the deduction on that in solution on the basis of the results of the visible absorption. From shifts in the C=O frequency[5] of the acyl group for *o*-chloro- and *o*-methoxy-substitutes, however, it seems probable that such twisting of the benzene ring does not arise on the molecule in solid, this being different from the molecule in solution. Though the benzene ring of the *o*-chloro- or *o*-methoxy-substitute in solution has been twisted by repulsion between the *o*-chloro or *o*-methoxy and the carbonyl group in the acyl group, such twisting may be suppressed in a solid where the molecules are paked closely. From the result of infrared absorption, it seems likely that for the *o*-amino-substitute in solid the benzene ring also does not twist, this being identical with the deduction on its molecular structure in solution on the basis of the results of the visible absorption.

Relative Difficulties of Vatting.—It has been concluded that from the interpretation of visible absorption for the acylaminoanthraquinone series, an electron density of the quinone-type carbonyl group within the chromophoric system decreases in the order of 1,4-, 1,8- and 1,5-isomers, and that it decreases in the order of 1,4- and 1,5-isomers from examinations of their infrared absorption. From both these bits of information and a reduction mechanism of anthraquinone[14], it is deduced that difficulty of reduction, namely difficulty of vatting, should naturally increase in the order of 1,4-, 1,8- and 1,5-isomers. The result has also been obtained from our experiments[2-4] showing that difficulty of vatting increases in the order of 1,4-, 1,8- and 1,5-isomers and vatting of the 1,8-isomer is no more difficult than vatting of the 1,4-isomer.

The result has been obtained from our experiments[2-4] that, for each seris of 1,4-, 1,5- and 1,8-diacylaminoanthraquinones, the effect of X or Y on the difficulty of vatting increases in the order of *p*-$SO_2N(Me)_2$, *m*-$SO_2N(Me)_2$, *m*-OMe, *m*-Cl, *p*-OMe, *p*-Cl, *m*-NO_2, *p*-NO_2. But difficulties of vatting of *m*-methoxy-, *m*-chloro- and *p*-methoxy-substitutes have been of much the same degree as that of the non-substitute and those of dimethylsulfamyl-substitutes have been especially small[2-4]. It is known that the relative difficulty of vatting, namely the relative difficulty of reduction,

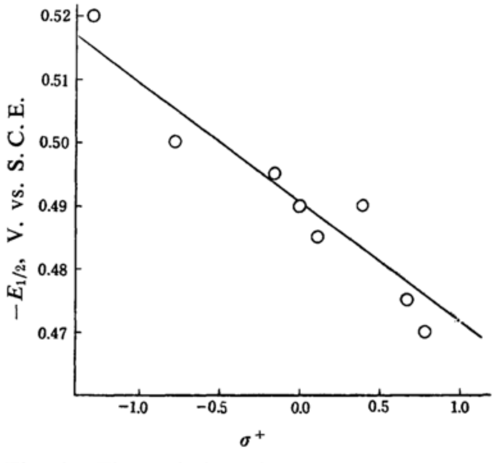

Fig. 4. The relationship between the first half-wave potential ($-E_{1/2}$) in ethanol and Brown's σ^+ value on the 1-acylaminoanthraquinone series.

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[14] T. Vickerstaff, "Physical Chemistry of Dyeing", Oliver & Boyd, London (1954), p. 282.

is dependent on both the magnitude of the reduction potential and the degree of the rate of reduction[14]. For the reduction potential, shifts of the reduction potential for 2-substitutes of 1,4-naphthoquinone or for 3-substitutes of phenanthrenquinone were in harmony with Hammett's rule[2], and a relationship between the first half-wave potentials of 1-acylaminoanthraquinone series and Brown's σ^+ values were also in accordance with Hammett's rule, as indicated in Fig. 4. From these results, there seems likely to be a correlation between the magnitude of the reduction potential and Hammett's σ or Brown's σ^+ value of the substituent for each series of acylaminoanthraquinones. On the contrary, from our results described above, it is evident that the effect of X or Y on the difficulty of vatting has been dependent not only on Hammett's σ or Brown's σ^+ value but also on the hydrophilic or hydrophobic property of X or Y. Therefore, it seems likely that for each series the relative difficulty of vatting is dependent on both the magnitude of the reduction potential and the degree of the rate of reduction, and that the rate of reduction bears a relation to the hydrophilic or hydrophobic property of X or Y.

Color Tones of Vat Solutions. — For leuco salts of these dyes, as two electron-donating substituents (O^-) occupy 9- and 10-positions where they have the maximum conjugation with the anthracene nucleus, the effect of these substituents is considerably greater than that of such substituents as acyl groups occupying the other positions. Therefore, the entire visible absorption curve, that is, color tones of vat solution for all of 1,4-, 1,5- and 1,8-diacylaminoanthraquinone series should be similar to one another. Such deduction has been consistent with our results[2-4], that is, the color tones of vat solution for all of them, except for di-*o*-substitutes, were from reddish violet-blue to reddish violet. Waters[15] and Venkataraman[16] also reported that for the vat solutions of anthraquinone, aminoanthraquinone, acylaminoanthraquinone and others the visible absorption curves with maximum absorption bands at 425 and 515 mμ were given, being approximately similar to one another.

Shades of Dyes.—The 1,4-diacylaminoanthraquinone series was a red dye, and 1,5- and 1,8-derivatives were yellow dyes but the shade of the latter on cotton was somewhat more bathochromic than that of the corresponding isomer of the former[2-4]. For all of the dyes with a nitro group as X or Y, the shades on cotton were from brown to intensely brownish on account of the amino group (reduction of the nitro group)[2-4]. The fact that the shade is hypsochromic in the order of 1,4-, 1,8- and 1,5-isomers, is explained in the same way by electronic interpretations on shifts in visible absorption bands for these dyes in solution. It was admitted that for each series of diacylaminoanthraquinones a shade of the XY type*** was in the middle between shades of the corresponding XX type and of the YY type, and this fact has shown that the effects of X and Y on the shift of the shade are additive. An electron-donating substituent in the acyl group causes the bathochromic shift of the shade and the reverse is found for electron-attracting substituents. Though *p*- and *m*-dimethylsulfamyl groups were found to be intensely electron-attracting from examinations of the visible absorption, the shades of dyes with these groups as X or Y have merely shown a change from the weak hypsochromic to the weak bathochromic shift. For 1,4- and 1,5-diacylaminoanthraquinone series, an effect of X or Y on enhancement of brilliance of the shade has been shown to be greater in the *m*- than in the *p*-position within the acyl group, as described in the PB Report[17], but such a difference has not been found for the 1,8-derivative. Generally speaking, the degree of brilliance on the shade of the XY type for each series of diacylaminoanthraquinones was higher than that of the corresponding XX or YY type.

It is known that adsorption of leuco vat dyes on cellulose is dependent on both their affinity and rate of diffusion[18], but as the rate of diffusion may be independent of a kind of X or Y for the acylaminoanthraquinone series, it seems likely that adsorption of leuco acylaminoanthraquinones is dependent on their affinity, and, therefore, the greater the affinity is, the greater is the depth of the shade. From affinities of some acylaminoanthraquinones for cotton, it has been concluded that for any one of these series there is little difference in affinity between the *m*- and *p*-substitutes but their affinities are greater than that of a non-substitute and a great reduction in affinity is shown on the *o*-substitutes[8,18]. From these bits of information, the depth of the shade of the non-substitute should be less than those of *m*- and *p*-substitutes and those of the *o*-substitutes should be especially small for each series. Such deductions have been consistent with our results[2-4] obtained from comparison

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[15] E. Waters, *J. Soc. Dyers Colorists*, **66**, 544 (1950).

[16] M. R. Padhye, N. R. Rao and K. Venkataraman, *J. Sci. Ind. Research (India)*, **13B**, 759 (1954); *Chem. Abstr.*, **49**, 15836 (1955).

*** The XX or YY type denotes the diacylaminoanthraquinone with the same two acyl groups and the XY type that with two different acyl groups.

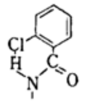
[17] BIOS 987 (PB 75860) p. 185.

[18] T. Vickerstaff, loc. cit., p. 299.

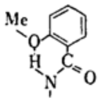
with the depth of the shade for many sets of the same shade. It is known that there is a definite correlation between affinity and molecular weight for these dyes, except for *o*-substitutes[8,18], but for dyes with a dimethylsulfamyl group as X or Y, the depth of the shade has been less in spite of the increase of molecular weight with the increasing surface area. This fact is due to a reduction of van der Waals force based on a decreasing coplanarity which is attributed to the bulky volume of the dimethylsulfamyl group.

***o*-Substitutes.**—It has been known from our experiments[2-4] that vatting of *o*-substitutes is more difficult than for *m*- and *p*-substitutes and the color tones of the vat solution for the former are more hypsochromic and pale than for the latter, and the former has dyed cotton with more difficulty.

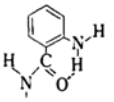
From interpretations of visible absorption bands for *o*-substitutes, it has been concluded that mesomeric shifts of electrons within their chromophoric system are suppressed by the *o*-substituents, namely the *o*-substituents lower the electron density of the quinone-type carbonyl group. In consideration of both this fact and the vatting mechanism of *o*-substitutes, it is natural that these dyes have increasing difficulty in vatting, as described above. For leuco *o*-substitutes the hypsochromic shifts in the color tone of their vat solutions, described above, are attributed to the reduced conjugation between the anthracene nucleus and *o*-substituted benzoyl groups, and the palenen of vat solutions may be due to a decrease in an effective area of the π-electron system for *o*-substitutes. For *o*-chloro- and *o*-methoxybenzoylaminoanthraquinones, Valentin[19] has partially attributed their reduced affinities to internal chelation within acylamido groups, as indicated in Va and Vb, but the reduced affinity of *o*-methylbenzoylaminoanthraquinone[8,18] can not be explained satisfactorily from his suggestion, and the presence of the internal chelation is inconsistent with the information about the molecular structure obtained from their visible absorption. As *o*-substituents make it difficult for the *o*-substitutes to attain a planar configuration as indicated by this information, these dyes may dye cotton with diffiiculty, as described above, on account of the reduction of van der Waals force with the decreased affinity.



Va



Vb

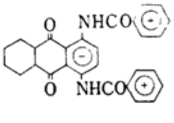


Vc

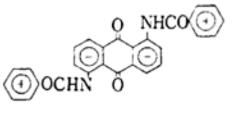
From interpretations on their visible absorption, it seems likely that *o*-amino-substitutes (reduction of the *o*-nitro-substitutes) have maintained coplanarity of the molecule, but the *o*-aminosubstitutes have also dyed cotton with difficulty. These results may be taken to show that the *o*-amino group prevents the hydrogen bond formation between the amido group and the cellulose hydroxyl group on account either of the steric hindrance of the *o*-amino group or the internal chelation as indicated in Vc.

Light Fastness. — Several relations between chemical constitutions of 1, 4-, 1, 5- and 1, 8-diacylaminoanthraquinone series and their light fastness have been drawn from the results[2-4] of the light fastness test for them. In the first place, grades of light fastness on cotton for 1, 4-, 1, 5- and 1, 8-dibenzoylaminoanthraquinones were 7, 6 and 5, respectively. The light fastness of the diacylaminoanthraquinone series on cotton has generally become lower in the order of 1, 4-, 1, 5- and 1, 8-isomers. The shades of these dyes on cotton, except for *p*-substitutes of the 1, 4-diacylaminoanthraquinone series, have not shown fading, but have shown a sign of turning brown under sunlight. For 1, 5- and 1, 8-diacylaminoanthraquinone series the light fastness of *p*-substitutes was generally higher than that of corresponding *m*-substitutes, which was higher than that of corresponding *o*-substitutes for each series of 1, 4-, 1, 5- and 1, 8-diacylaminoanthraquinones. For each series of them, in comparison with the light fastness of a non-substitute, the dyes with a chloro group as X have shown almost no lowering, but the dyes with a methoxy or dimethylsulfamyl group have shown slight lowering, and all of the dyes with a nitro group (an amino group on cotton) evident lowering.

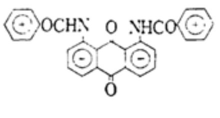
It is know that for a group of dyes of the



VIa



VIb



VIc

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[19] L. Valentin, *J. Soc. Dyers Colorists*, **72**, 286 (1956).

same type, for example simple azo dyes, in general, the greater the difference is of an electron density on two parts within a molecule of the dye, the higher the light fastness of the dye is. For dibenzoylaminoanthraquinones it seems likely that an electron density of the benzene ring in the benzoyl group is lower than that of the benzene ring within the anthraquinone nucleus, as indicated in VIa, VIb and VIc, from both pieces of information about mesomeric shifts of electrons within the chromophoric systems and examinations of some reactions of the dyes with reagents. For 1, 4-dibenzoylaminoanthraquinone two chromophoric systems hold one benzene ring within the anthraquinone nucleus in common, but for 1, 5- and 1, 8-dibenzoylaminoanthraquinones two chromophoric systems bear relations with different benzene rings in the anthraquinone nucleus respectively. The difference between electron densities of the benzene ring in the benzoyl group and of the benzene ring in the anthraquinone nucleus for the 1, 4-derivative should therefore be greater than for the 1, 5- or 1, 8-derivative. From interpretations of both visible and infrared absorption for 1, 5- and 1, 8-derivatives, it has been concluded that an electron density of the quinone-type carbonyl group on the peri-position of the benzoylamido group for the latter is somewhat higher than for the former. As two chromophoric systems of the 1, 8-derivative holding one carbonyl group in common are cross conjugation, mesomeric shifts of electrons within them are suppressed by each other; but, on the other hand, two chromophoric systems of the 1, 5-derivative bear almost no relation to each other. The extent of the mesomeric shift of electrons within one chromophoric system for the former is therefore less than for the latter, and then the difference between electron densities of the benzene ring in the benzoyl group and of the benzene ring in the anthraquinone nucleus for the former is less than for the latter. Finally, the difference between electron densities of two benzene rings decreases in the order of 1, 4-, 1, 5- and 1, 8-isomers, and this order may be responsible for the lowering of light fastness in the order of 1, 4-, 1, 5- and 1, 8-isomers, described above. An alternative possibility is that the 1, 5-isomer being trans-form it probably packs more compactly than the 1, 8-isomer which is in cis-form in the solid of the dye within the fiber, and also that the light fastness of the former may be higher than that of the latter.

The effects of Cl, OMe or NH_2 as X on light fastness, described above, were similar to the results[20] already known concerning many dyes. Though a dimethylsulfamyl group is intensely electron-attracting, shades of the dyes with this group as X or Y have only shown changes from weak bathochromic to weak hypsochromic shifts in comparison with the shade of the non-substitute, and further the dimethylsulfamyl group has an appearance of a weak electron-attracting or weak electron-donating group in these cases. This fact may bear some relation to the lowering of the light fastness of these dyes described above. The lowering of light fastness may be due to the fact that these dyes can not pack compactly in the solid of the dye within the fibre owing to the bulky volume of the dimethylsulfamyl group.

The authors wish to express their sincere thanks to Professor Yoshio Nagai and Dr. Shimpachiro Kato of Tokyo University for their helpful suggestions and encouragement in the course of this work. They also wish to thank the Tokuyama Research Laboratory of Idemitsu Kōsan Co. for infrared measurements.

Department of Chemistry
Faculty of Literature and Science
Yamaguchi University
Ushirogawara, Yamaguchi-shi

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[20] A. Gebhard, ibid., 25, 305 (1909).