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Abstract

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Comparative Study of the Affinity of Direct Azo Dyes—Derivatives of Diphenyl and *para*-Terphenyl—for Cellulosic Cotton Fiber

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The question of the relationship between the structure of azo dyes and their affinity for cellulose fiber has long attracted the attention of many investigators; moreover, the published works on this question have been devoted mainly to the study of dyes of the benzidine series, containing a diphenyl nucleus in their molecules.

A. E. Porai-Koshits (1) noted the positive influence exerted by the unsaturation of dye molecules on their affinity for vegetable fibers. According to Schirm' s conjugation theory (2), applicable to most direct dyes, for a dye to exhibit substantive properties it is necessary that its molecules contain a long chain of conjugated double bonds; then the molecules become unsaturated and are readily fixed on the cellulose fiber.

It may be regarded as established that the substantivity of dyes is to a considerable extent connected with their spatial structure: the molecules of direct dyes must be planar (3), or assume a planar structure upon interaction with the cellulose fiber (4).

Finally, an important condition of substantivity is the possibility of forming not fewer than two hydrogen bonds between the dye molecules and the hydroxyl groups of cellulose (5). A number of works indicate that, in the molecules of direct dyes, the distance between groups capable of forming hydrogen bonds should be close to the identity period of cellulose, which is equal to 10.3 Å (6). This condition is well satisfied by the structure of benzidine dyes. At the same time, Robinson (7), using improved atomic models that make it possible to take into account various deformations of dye molecules, showed that this distance is not of essential significance, since hydrogen bonds can be formed at almost any point of the cellulose chain.

On the basis of a comparative study of disazo dyes obtained from *para*-phenylenediamine (I) and benzidine (II)

$$\mathrm{R-N=N-}\rangle\langle\mathrm{-N=N-R}$$

(I)

$$R-N=N-\rangle\langle\rangle\langle-N=N-R^{*}$$

(II)

it was shown that the first of these dyes, containing shorter chains of conjugated double bonds, are less substantive (8,9). However, the investigations of Bogoslovskii (10) and Filippichev (9) revealed that an increase in the chains of conjugated double bonds contributes to an increase in sub-

substantivity only up to a certain limit, after which the substantivity does not increase and may even decrease somewhat. Thus, in a comparative study of the substantivity of dyes I, II and the corresponding disazo dye III

$$R-N=N-\langle\text{ benzene rings }\rangle-N=N-R,$$

III

obtained from 4,4‴-diaminquaterphenyl, it proved that the latter is inferior in substantivity to the benzidine dye, despite the presence in its molecules of a longer chain of conjugated double bonds (11). In this series, investigated by Bogoslovskii and Chaplina, dye IV is absent,

$$R-N=N-\langle\text{ three benzene rings }\rangle-N=N-R,$$

IV

which contains three benzene rings between the azo groups and is a derivative of *p*-terphenyl. Dyes—terphenyl derivatives—were studied by Allen and Pingert (12), who reported on their substantive properties; a brief indication of the substantivity of dyes—terphenyl derivatives—is also contained in Hodgson' s work (13), but these studies were only qualitative in character. At the same time, investigation of dyes—*p*-terphenyl derivatives—makes it possible to trace the influence of the successive accumulation of benzene rings and, thereby, of the increase in the chain of conjugated double bonds, on the affinity of dyes for cellulose fiber. It also makes it possible to establish how significant, in the present case,

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* *R* —azo component.

is the mutual arrangement of groups capable of forming hydrogen bonds with cellulose, and the distance between them. Therefore, having at our disposal a method (14) based on determining the affinity of dyes under conditions of equilibrium dyeing, which makes it possible objectively to evaluate the affinity of dyes for cellulose fiber, we considered it interesting to compare the affinity of certain benzidine dyes and the corresponding dyes—*p*-terphenyl derivatives. In addition, it seemed useful to us, in the course of this study, to trace the influence of the nature of the azo component on the magnitude of the affinity of the above-mentioned dyes.

Table 1

Dye	Affinity $-\Delta Z$, kcal/mol, 100° C	Affinity $-\Delta Z$, kcal/mol, 80° C	Heat of dyeing ΔH, kcal/mol	Entropy change $-\Delta S$, cal/mol · deg
Benzidine → 2 mol. naphthionic acid	5.76	5.90	8.7	8.0
Benzidine → 2 mol. γ-acid	5.40	6.06	16.5	26.8
Benzidine → 2 mol. G-acid	2.18	2.39	6.09	10.5
Benzidine → 2 mol. ϵ-acid	2.78	3.03	7.44	12.5
Benzidine → 2 mol. chromotropic acid	3.82	4.90	23.96	54.0
Benzidine → 2 mol. K-acid	4.18	4.47	9.59	14.5
Benzidine → 2 mol. Ash-acid	3.73	4.45	16.5	34.3
Benzidine → 2 mol. Chicago CC-acid	3.8	4.58	18.35	39.0

Dye	Affinity $-\Delta Z$, kcal/mol, 100° C	Affinity $-\Delta Z$, kcal/mol, 80° C	Heat of dyeing ΔH, kcal/mol	Entropy change $-\Delta S$, cal/mol · deg
4,4″-Diaminoterphenyl → 2 mol. ϵ-acid	4.29	4.89	15.48	30.0
4,4″-Diaminoterphenyl → 2 mol. Ash-acid	5.26	6.00	19.06	37.0
4,4″-Diaminoterphenyl → 2 mol. Chicago CC-acid	5.39	6.31	22.55	43.3

At the same time we had in mind that, up to the present, attention has been directed mainly to the influence of the structure of the diazo component on the substantivity of dyes, while considerably less attention has been paid to the influence of the azo component. Among works devoted to the study of the relationship between the structure of the azo component and substantivity, one may note, for example, the work of Levy, who carried out a comparative study of dyes from M-acid and its isomeric γ-acid (15); the influence of certain azo components on substantivity was also studied by Ruggli and Leupi-

by Filipichev (9) and other investigators. We compared the properties of dyes from benzidine containing eight different azo components and of dyes—derivatives of *p*-terphenyl—with three azo components. Table 1 gives data on affinity, heat of dyeing, and entropy change for all these dyes; moreover, the data on the properties of certain benzidine dyes (azo components: Ash-, γ-, and naphthionic acids) are given on the basis of studies previously carried out by Moryganov and Mel' nikov (17).

The 4,4″-diaminoterphenyl required for the synthesis of the dyes was obtained by a known procedure (18). Diazotization of this amine was carried out with sodium nitrite in a hydrochloric-acid medium. Azo coupling in the preparation of all dyes, with the exception of Congo Red, was carried out in an alkaline medium. The dyes were purified from possible admixtures of monoazo dyes by chromatography on alumina and were freed from mineral impurities by the acetate method (19). Analysis of the dyes was carried out according to a previously published method (20). In determining the affinity of the dyes for cellulose, the heat of dyeing, and the entropy change, we used the above-mentioned method (21).

The data presented in Table 1 show that in all cases the introduction of an additional benzene ring into the dye molecule increases its affinity for cellulose cotton fiber; moreover, for dyes with Chicago CC- and ϵ-acid azo components, the affinity increases at 80° somewhat more than at 100°. The unequal increase in affinity at the two temperatures can apparently be explained by the greater tendency of these dyes to aggregate when the temperature is lowered. Consequently, in the present case, the magnitude of the affinity of the dyes for cellulose will be determined not only by the manifestation of interaction forces between them, but also by large entropy changes associated with the transition of individual dye molecules into aggregates. In the dyeing process itself this is manifested in the fact that the fiber can sorb a larger amount of dye than is determined by the nature of the forces acting between the dye and the fiber, since the fiber can absorb not only individual dye ions but also their aggregates.

Thus, lengthening the chain of conjugated double bonds, leading to an increase in the hydrophobic surface and to enhanced polarization of the dye molecules, in the present case leads to an increase in affinity for cellulose fiber, despite the fact that in the molecules of the dyes—terphenyl derivatives—the distance between the groups forming hydrogen bonds with cellulose does not coincide with the identity period of cellulose.

When the benzidine dyes with different azo components are compared with one another, the low affinity of the dyes from Γ- and ϵ-acids attracts attention. The dye from 4,4″-diaminoterphenyl with the ϵ-acid azo component also has a lower affinity for cellulose fiber than do the other dyes—terphenyl derivatives. This phenomenon is apparently connected with the unfavorable mutual arrangement in the dye molecules of the groups forming hydrogen bonds with cellulose and of the groups responsible for the solubility of the dye: the negatively charged SO_3^- groups of the dye anions hinder the formation of hydrogen bonds between the oxy groups situated close to them and the negatively charged cellulose (dyes with the ϵ-acid azo component). It is also possible that the reason for the reduced affinity of dyes from Γ- and ϵ-acids is the presence, in the peri positions of the naphthalene nuclei, of such bulky substituents as sulfo groups, which may lead to steric hindrance in the dye molecules and to the associated decrease in affinity.

Comparison of isomeric benzidine dyes with azo components—Ash-, Chicago CC-, and K-acids—shows that the different arrangement of sulfo groups in the molecules of these dyes does not exert a large influence on affinity for plant fiber; they differ little in their affin—

and dyes of the terphenyl series with azo components of Ash and Chicago CC acids. Benzidine dyes with azo components of Ash acid and chromotropic acid also differ little from one another: replacement of an amino group by a hydroxyl group, in the present case, has little effect on the magnitude of the affinity.

Finally, it should be noted that dyes from naphthionic and γ-acids, containing fewer sulfo groups than all the other benzidine dyes, possess the greatest affinity. Here, apparently, the difference in the solubility of the dyes, associated with the number of sulfo groups in their molecules, has an effect. It is possible that here the absence, in the naphthalene nuclei at position 8, of any substituents whatsoever—even such comparatively small ones in volume as amino groups—which may influence to a greater or lesser degree the spatial structure of the dyes, is also of importance.

Interpretation of the data on the heats of dyeing and entropy changes given in Table 1 is at present difficult for us, since the physicochemical factors determining the values ΔH and $-\Delta S$ have not yet been sufficiently clarified. Our point of view on the question of the physical meaning of these quantities is set forth in one of the above-mentioned works (17).

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Note: Figure translations are in progress. See original paper for figures.