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EFFECT OF THE TRIFLUOROMETHYLSULPHONYL GROUP ON THE COLOUR OF DIMETHYLAMINOAZO DYES

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SUMMARY

The comparison of the electronic spectra of mono- and di-substituted dimethylaminoazo dyes with electron-withdrawing substituents CF_3SO_2 and NO_2 shows that in para-*substituted dyes the chromophore chain length plays the main role whereas in* ortho-*substituted dyes steric effects are essential. In di-substituted dyes account must be taken of the positions of both substituents in the benzene ring. The halochromity indices of dyes are directly dependent on the electronic effects of substituents.*

1. INTRODUCTION

Previously we[1,2] have established the regularities connecting the electronic nature of substituents with their influence on the colour of dialkylaminoazo dyes. To obtain deeply coloured dyes, the introduction of nitro-groups is widely used. The trifluoromethylsulphonyl group is a stronger electron-withdrawing substituent than a nitro-group (σ_p constants are 0·96 and 0·78, respectively),[3] and the comparison of electronic spectra of dimethylaminoazobenzenes containing the CF_3SO_2 group with those of their nitro analogues is of interest. For this purpose compounds obtained by us formerly have been used and relevant new substituted dyes have been synthesized.

2. DISCUSSION OF RESULTS

The dyes studied and relevant spectrophotometric data are shown in Table 1. Comparison of the absorption maxima of *meta*-substituted dyes shows that the

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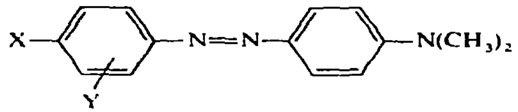
trifluoromethylsulphonyl group (Dye (1)) produces a blue shift of 9 nm relative to the nitro-group (Dye (2)). This bathochromic shift of the absorption maximum is in harmony with the inductive effect of these substituents (SO_2CF_3, $\sigma_I = 0{\cdot}73$; NO_2, $\sigma_I = 0{\cdot}56$).

The absorption maxima of *para*-substituted dimethylaminoazo dyes with CF_3SO_2 and NO_2 groups, (Dyes (3) and (4)), are close to each other. The *p*-NO_2-derivative of N_1N-dioxyethylamino-*m*-toluidine shows a bathochromic shift of 8 nm relative to that of the *p*-CF_3SO_2 derivative.[1] The difluoromethylsulphonyl and the fluorosulphonyl groups are also more electron-withdrawing than the nitro-group (SO_2CHF_2, $\sigma_p = 0{\cdot}86$;[4,5] SO_2F, $\sigma_p = 0{\cdot}88$[1,6]). However, they produce a hypsochromic shift of the absorption maximum of 12 nm relative to that of 4′-nitrodimethylaminoazobenzene. Stronger electron-withdrawing substituents CF_3SO_2, CHF_2SO_2, FSO_2 should cause much deeper colour in dyes than a nitro-group. In fact, this is not observed, because sulphur-containing substituents, unlike the nitro-group, are tetrahedral, and for this reason the conjugation chain of the dye with these groups shortens. Probably conjugation does not extend to the oxygen atoms and is restricted by the sulphur atom participating in the conjugation due to its d-orbitals.

TABLE 1
ABSORPTION MAXIMA OF THE DIMETHYLAMINOAZODYES



Dye	*X*	*Y*	λ_{max}, *nm*		Δ
			Ethanol	*Ethanol + HCl*	
1	H	*m*-SO_2CF_3	443	498	55
2	H	*m*-NO_2	434	504	70
3	SO_2CF_3	H	476	500	24
4	NO_2	H	475	508	33
5	H	*o*-SO_2CF_3	466	490	24
6	H	*o*-NO_2	440	509	69
7	NO_2	*o*-SO_2CF_3	555	480	−75
8	SO_2CF_3	*o*-SO_2CF_3	552	474	−78
9	NO_2	*o*-NO_2	516	498	−18
10	SO_2CF_3	*m*-NO_2	522	490	−32
11	SO_2CF_3	*o*-NO_2	525	489	−36
12	NO_2	*m*-SO_2CF_3	500	500	0

The dye containing the CF_3SO_2 group in the *ortho* position is significantly more deeply coloured (shift > 20 nm) than the dye with the *o*-NO_2 group (Dye (6)) because steric factors play an important role in the electronic effect of a nitro-group. In the *ortho* position it seems to be twisted from the plane of the chromophore and therefore exhibits only its inductive effect. This conclusion is confirmed by the fact that the absorption maxima of the *ortho-* and *meta*-dimethylaminoazo dyes are close to each other whereas the halochromicity ($\Delta = \lambda_{max}$ (acid) $- \lambda_{max}$ (neutral)), which correlate well with the electronic effect of substituents, are the same in both cases. In addition, the σ_0 value found graphically for a nitro-group is lower than the σ_0 value of the much less electron-withdrawing CF_3 group.[2]

In the case of a trifluoromethylsulphonyl group the breakdown of coplanarity does not lead to an essential decrease of the electron-withdrawing effect. The conjugation of a CF_3SO_2 group with the chromophore system of the dye is maintained due to the fact that conjugation effects involving the third row elements do not necessarily require a coplanar configuration of a substituent and a chromophore system.

Although the absorption maximum of the dye with the CF_3SO_2 group in the *ortho* position is shifted bathochromically (10 nm) relative to that of the *para* isomer, the halochromicity indices of both dyes are the same due to shortening of the conjugation chain.

Considering the effects of the position of different substituents on the colour of mono-substituted azo dyes, it is possible to make predictions regarding the colour of di-substituted dyes. Thus, the dye (7) containing p-NO_2 and o-CF_3SO_2 groups should be the deepest in colour.

In fact, it shows an absorption maximum at 555 nm. The dye (8) with two CF_3SO_2 groups in the *ortho* and *para* positions shows a hypsochromic shift of the absorption maximum of 3 nm whereas the absorption maximum of 2′,4′-dinitrodimethylaminoazobenzene is much more shifted (40 nm) to shorter wavelengths. The absorption maxima and halochromicity indices of dyes containing the p-CF_3SO_2 group and the m- or o-NO_2 group are close to each other because in both cases an NO_2-group reveals only its inductive effect. The largest hypsochromic shift of the absorption maximum is observed for the dye (12) with p-NO_2 and m-CF_3SO_2 groups. The bulky trifluoromethylsulphonyl group seems to influence to a large extent the conjugation of the neighbouring nitro-group with the chromophore system of the dye; thus in this case the electronic effect of the nitro-group is practically reduced to its inductive effect. It is interesting that the colour of this dye remains unchanged in the presence of an acid ($\Delta = 0$), although a proton adds to the β-nitrogen of the azo group, as is evidenced by the increase in the extinction coefficient.[1]

The halochromicity indices (Δ) of dyes directly depend on the electronic effects of substituents in all considered cases. The dye (8) with two trifluoromethylsulphonyl groups is coloured a little more deeply than dye (7) with p-NO_2 and o-CF_3SO_2 groups; however, its halochromicity index is the most negative of all.

The regularities in the influence of the electron-withdrawing substituents NO_2 and CF_3SO_2, widely used for deeply coloured dyes, which have been established for model dimethylaminoazobenzenes facilitate the synthesis of dyes of different classes with desired properties.

3. EXPERIMENTAL

Dyes (**1**)–(**6**), (**9**), (**10**) and (**12**) have been described earlier.[1,2] Dyes (**7**), (**8**) and (**11**) were prepared by diazotization of the corresponding amine in nitrosylsulphuric acid and coupling with dimethylaniline according to the technique given elsewhere.[1]

2'-Trifluoromethylsulphonyl-4'-nitrodimethylaminoazobenzene (Dye (**7**)) was obtained from 2-trifluoromethylsulphonyl-4-nitroaniline.[7] Yield was 43%, m.p. 216–218 °C (ethanol). Analysis found (%): N 14·20; 14·35. Calculated for $C_{15}H_{13}F_3N_4O_4S$: N, 13·93.

2', 4'-Bis(trifluoromethylsulphonyl)dimethylaminoazobenzene (Dye (**8**)) was obtained from 2,4-bis(trifluoromethylsulphonyl)aniline.[8] Yield was 54%, m.p. 169–171 °C (hexane). Analysis found (%): F 22·58; 22·72. Calculated for $C_{16}H_{13}F_6N_3O_4S_2$: F, 23·30.

2'-Nitro-4'-trifluoromethylsulphonyldimethylaminoazobenzene (Dye (**11**)) was obtained from 2-nitro-4-trifluoromethylsulphonylaniline.[9] Yield was 66%, m.p. 173–175 °C (ethanol). Analysis found (%): N 14·14; 14·25. Calculated for $C_{15}H_{13}F_3N_4O_4S$: N, 13·93.

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