SYNTHESIS AND ELECTRONIC ABSORPTION SPECTRA OF SOME AZO DYES AND THEIR ANALOGUES AZOMETHINES

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Azo dyes are the most important class of dyes that have commercial application. Their colour range is usually from yellow to red for simple aromatic azo dyes (Griffiths 1984). The colour of azo dyes can be further red shifted by using heterocyclic amines as the diazo components. By using the appropriate diazo-component, violet, blue, green and IR-active azo dyes are prepared (Gordon and Gregory 1983; Bello and Griffiths 1986). On the other hand Schiff bases normally range in colour from yellow to red (Chalkely 1929). The present paper describes the absorption spectra of four azo dyes *1a-d* and their analogous Schiff bases *2a-d* and *3a-d*.

Azo dyes *1a-d* were prepared by the well-established procedure (Vogel 1946). Schiff bases *2a-b* were prepared by condensing 4-N,N-dimethylaminobenzaldehyde and the appropriate aniline. On the other hand dyes *3a-d* were prepared by condensing N,N-dimethyl-1,4-phenylendia-mine and the appropriate aldehydes. The physical data of synthesized compounds are summarized in Table 1.

Table 1
Synthetic and IR data of dyes 1, 2 and 3

| Dye No.	Yield (%)	M.P. (°C)	Formula*	ν_{max} (cm^{-1}) -N=N-	-C=N-	NO$_2$
1a	65	73	$C_{14}H_{15}N_3$	1604	1519	1368
1b	98	105	$C_{14}H_{14}N_4O_2$	1603	1529	1370
1c	40	121	$C_{14}H_{14}N_4O_2$	1604	1524	1369
1d	17	190	$C_{14}H_{14}N_4O_2$	1602	1526	1367
2a	76	75	$C_{15}H_{15}N_2$	1601	1531	1371
2b	99	65	$C_{15}H_{14}N_3O_2$	1627	1507	1372
2c	96	83	$C_{15}H_{14}N_3O_2$	1621	1520	1351
2d	95	204	$C_{15}H_{14}N_3O_2$	1604	1537	1373
3a	92	80	$C_{15}H_{15}N_2$	1619	1517	1360
3b	96	180	$C_{15}H_{14}N_3O_2$	1615	1519	1340
3c	95	130	$C_{15}H_{14}N_3O_2$	1617	1527	1356
3d	96	185	$C_{15}H_{14}N_3O_2$	1618	1516	1341

* All compounds gave satisfactory elemental analysis
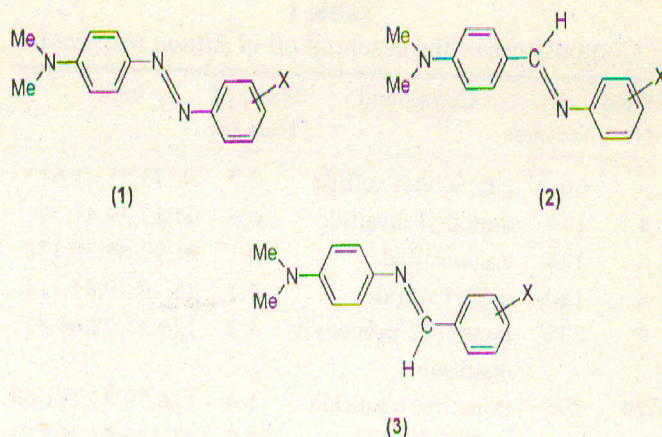
UV-Visible Absorption Spectroscopic Properties. Ultraviolet-Visible absorption spectroscopic data for dyes 1,2 and 3 are summarized in Table 2. Absorption maxima in various solvents are also given.

Schiff Bases 2a-d. The parent dye *2a* showed λ_{max} at 355 nm in ethanol, while the introduction of electron withdrawing group such as nitro group gave a significant bathochromic shift, for example dyes *2b-d* absorb at higher wavelengths when compared with dye *2a* (Table 1). The position of the nitro group in the phenyl ring has a remarkable influence on λ_{max}. In the dye series *2a-d* it is possible to assess the relative effectiveness of various nitro derivatives in producing a bathchromic shift and the sequence for λ_{max} values *2d> 2b > 2c >2a* is observed. Thus the substitution in position para to the azomethine (-CH=N-) is the most effective in producing a red shift. The dye series *2a-d* showed a negligible shift in λ_{max} as the solvent polarity increased.

Schiff's Bases 3a-d. *3a* showed λ_{max} at 378 nm in CHCl$_3$. The introduction of a nitro group to the ring B (4) causes a bathchromic shift as far as 455 nm for 4-NO$_2$ *3d*. The dye series *3a-d* showed the same order of relative effectiveness in producing a bathchromic shift as shown by the dye series *2a-d*.

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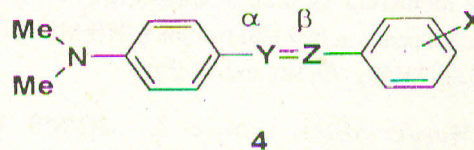
In the series *3a-d* increase in the solvent polarity did not show a remarkable shift on the absorption maxima.

It is interesting to compare the dyes *2a-d* and *3a-d*. Theoretical calculation (Griffiths 1981) using PPP-MO on donor-acceptor chromophores e.g. (4, Y=Z=N) predicted that replacement of a carbon atom at a starred position by a more electronegative heteroatom will cause a hypsochromic

Table 2
The absorption spectral data of synthesized dyes in various solvents

Dye No.	Toluene	CHCl$_3$	DCM	Acetone	CH$_3$CN	EtOH	EtOH+HCl
1a	355	355		384	352	359	516
1b	482	509		548	427	441	510
1c	434	486			435	435	518
1d	457	490		472	479	478	510
2a	350			350	353	355	
2b	390	396	393	404	402		
2c	362			358	360	64	
2d	395			398	399	394	
3a	378	368	378	375	381	375	
3b	425	424	420	411	408	414	
3c	396	396	395	392	391	394	
3d	446	455	454	423	442	444	

shift where as similar replacement at an unstarred position will causes a bathchromic shift. This prediction can be proved correct by comparing λ_{max} for dyes *2a-d* and *3a-d* (Table 2).

For example replacement of (CH) in 2d by nitrogen atom and the nitrogen by (CH) to give *3d* causes a bathchromic shift of 60 nm.

Azo dyes 1a-d. Further bathochromic shift is predicted to be achieved by replacing both atoms Y and Z in 4 by electronegative atoms. To verify that, we synthesized the azo dye series *1a-d*.

Dyes *1b-d* are more bathchromic than their azomethine analogues *2a-d* and *3a-d*.

In *1a-b* series the relative effectiveness of the acceptor is in the same order as for dyes *2a-d* and *3a-d* (Table 2).

Halochromism Effects of Dyes 1a-d. As common with all aminoazo dyes, the derivatives *1a-d* showed marked colour changes in solution in the presence of acids.

Halochromism in the aminoazo dyes is due to protonation of the azo group at the nitrogen atom more remote from the amino group e.g. azonium ion 5 (Scheme 1) and is usually accompanied by a large bathchromic shift (positive halo-chromism) (Yagupol's Kii and Gande's Man, 1965).
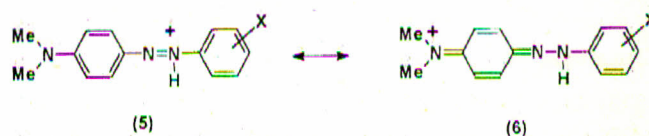
For dyes *1a-d*, the effect of substituents on the colour of azonium ion 5 is opposite to their effect on the neutral azo dyes *1a-d* Table2.

Key words: Azodyes, Azomethines, Schiff's bases.

References

Bello K A, Griffiths J 1986 Azo dyes with absorption bands in the near infrared. *J Chem Soc Chem Comm* 1639-1640.

Chalkley L 1929 Phototrop. *Chem Rev* **6** 217-279.

Gordon P F, Gregory P 1983 *Organic Chemistry in Colour.* Springer-Verlag, Berlin, Germany pp1-100.

Griffiths J 1981 Recent developments in the colour and constitution of organic. *Dyes Rev Prog Colouration,* **11** 37-57.

Griffiths J 1984 *Developments in the Chemistry and Technology of Organic Dyes.* Black Well Scientific Publications, UK, pp 55-120.

Vogel A 1946, *Practical Organic Chemistry.* Longman, London, UK, pp 623-624.

Yagupol's Kii L M, Gandel's Man L Z 1965 Negative halochromism of some dimethylaminoazobenzene derivatives. *J Gen Chem USSR* **35** 1992-1997.