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Merocyanines and *p*-Dialkylamino Styryl Dyes Derived from 1, 2, 6, 7—Dibenzoxanthone

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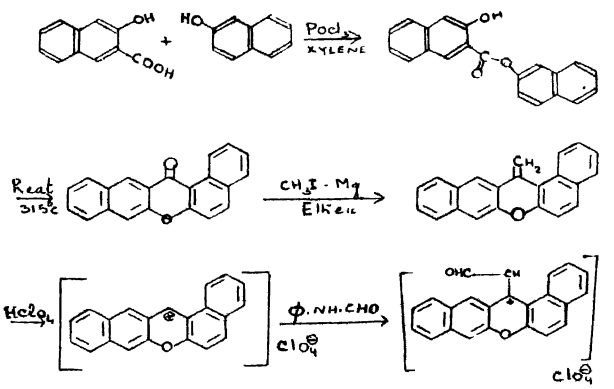
A number of merocyanines and *p*-dialkylamino styryl dyes have been prepared from 1, 2, 6, 7-dibenzoxanthone. Utilising the absorption maxima data of these dyes the relative order of acidities of ketomethylene compounds used in the synthesis of merocyanines have been studied. The influence of structural changes on absorption of the dialkylamino styryl dyes is also discussed.

In the present investigation a number of merocyanines ($n = 1$) and *p*-dialkylamino styryl dyes have been prepared from 1, 2, 6, 7-dibenzoxanthone. Their absorption spectra have been utilised in the evaluation of relative acidities of ketomethylene compounds.

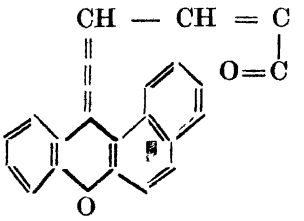
1, 2, 6, 7-dibenzoxanthone was prepared by the method of Kamal and Shoeb[1], starting from 2-hydroxy 3-naphthoic acid and *β*-naphthol. The 9-methylene compound was prepared by the Grignard reaction of the dibenzoxanthone by the method of Kamal (loc. cit.). The 9-methylene compound was then treated with perchloric acid in acetic acid medium to give 9-methylene xanthylium perchlorate. The 9-methylene xanthylium perchlorate was converted to the *w*-aldehyde perchlorate by treatment with formanilide in acetic anhydride. The reaction mechanism of the various steps may be represented as follows :—



For preparing the *p*-dialkylamino styryl dyes the quaternary perchlorate of 9-methylene dibenzoxanthone was condensed with *p*-dimethylamino benzaldehyde in presence of acetic anhydride. The merocyanines were prepared by condensing the *w*-aldehyde perchlorate of dibenzoxanthone with various ketomethylene compounds in presence of pyridine.

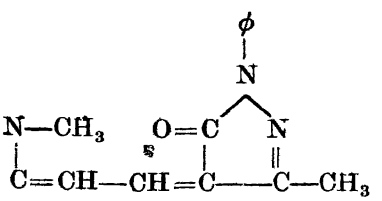
1. M. Kamal and H. Shoeb, *Tetrahedron* 1964, 483.

TABLE I



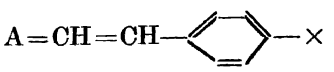
Nature of variable nuclei	Fixed Nucleus: Sym methin oxonol	Variable Nucleus: Sym trimethin cyanine	λ_{max} calculated mμ	λ_{max} obs. mμ	Deviation mμ
Pyrazolone	440	762	601	484	117
Rhodanine	452	762	657	517	140
Thiobarbituric acid	460	762	611	545	66
Thiohydantoin	520	762	641	476	165
Chroman 2 : 4-Dione	430	762	596	571	25
5 : 6 benzchroman-2 : 4 dione	430	762	596	574	22

TABLE II



Nature of nucleus A	Sym methin oxonol of B	Sym trimethin cyanine A	λ_{max} calcd. mμ	λ_{max} obs. mμ	Deviation mμ
Benzothiazole	440	565	502.5	490	12.5
Benzoxazole	440	480	460	447	13
Quinoline-2	440	610	525	523	2
Quinoline-4	440	710	575	587	−12
Benz(f)quinoline	440	630	535	533	2
4-Phenyl thiazole	440	565	502.5	500	2.5
Dibenzoxanthone	440	762	601	484	117

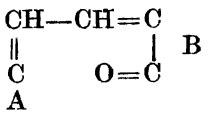
TABLE III



in 1, 2, 6, 7 dibenzoxanthone

Sl. No.	Nature of X	λ_{max} mμ	M.P. °C	% yield
1	*p*-dimethyl amino-	692	205	60
2	*p*-diethyl amino-	720	180	56
3	*p*-methoxy-	552	112	48

TABLE IV



Fixed Nucleus Variable nucleus.

Sl. No.	Nature of nucleus B	λ_{max} in mμ	% yield	M.P. °C
1	Pyrazolone	484	65	240
2	Rhodanine	507	62	198
3	Thiobarbituric Acid	545	55	240
4	Thiohydantoin	476	48	185
5	5 : 6 Benzchroman 2 : 4 dione	573	56	222
6	Chroman 2 : 4 dione	571	58	215

Utilising the absorption maxima data of merocyanine dyes derived from 1, 2, 6, 7-dibenzoxanthone the deviations of the individual merocyanines have been calculated[2–5]. These deviations have been used as a measure of relative acidity of different nuclei linked to one fixed basic nucleus through a chromophoric chain in a series of merocyanines (Brooker, loc. cit.).

2. L. G. S. Brooker, G. H. Keyls, R. H. Spraque, R. H. Vandy, E. Vanlarke, G. Vanzandt and F. L. White, *J. Amer. Chem. Soc.*, 1951, **53**, 5343.

3. L. G. S. Brooker, A. L. Skalar, H. W. J. Gussman, G. H. Keyls, A. L. Smith, R. H. Spraque, F. L. White and W. W. Williams, *J. Amer. Chem. Soc.*, 1945, **67**, 875.

4. M. K. Rout and B. K. Sabat, *J. Indian Chem. Soc.*, 1962, **39**, 103.

5. M. K. Rout, *J. Sci. Ind. Res.*, 1961, **2013**, 177.

The deviation values indicate that the relative acidity of six acidic nuclei lie in the order, 2, 3, 5, 6-Benzchroman-2,4-dione > chroman 2 : 4-dione > thiobarbituric acid > pyrazolone > rhodanine > thiohydantoin.

Similarly, the relative basicity of 1, 2, 6, 7 dibenzoxanthone has been calculated by the method of Brooker and coworkers[2,3] and the sequence confirms the following order.

Quinoline-4 > Benz(f) quinoline > 4-ph-thiazole > Benzothiazole > Benzoxazole > Dibenzoxanthone.

The styryl dye derived from dibenzoxanthone and *p*-dimethylamino benzaldehyde absorbs at a higher wave length than the dye obtained from anisaldehyde. This can neatly be explained by considering the energy differences between the resonating structures of these two types of styryl dyes.

EXPERIMENTAL

9-methylene 1, 2, 6, 7-dibenzoxanthone, 9-methylene xanthilium perchlorate and 9-methylene, 1, 2, 6, 7-dibenzo xanthilium *w*-aldehyde perchlorate were prepared by the method of Kamal and Shoeb[1].

The merocyanines and the styryl dyes were prepared by the method of Rout and co-workers[4,5].

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