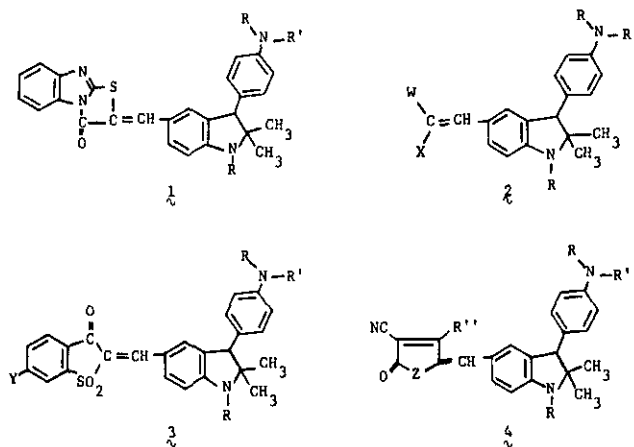


METHINE DYES FROM 1-ALKYL-3-[4-(DIALKYLAMINO)PHENYL]-2,3-DIHYDRO-
2,2-DIMETHYL-1H-INDOLE-5-CARBOXALDEHYDES

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Novel methine dyes (1-4) were synthesized by condensation of a variety of activated methylene compounds with 1-alkyl-3-[4-(dialkylamino)phenyl]-2,3-dihydro-2,2-dimethyl-1H-indole-5-carboxaldehydes. Many of these dyes were found to be very active in photoelectrophoretic migration imaging processes. The dyes were also tested in textile applications, but no advantages were found over conventional commercial methine dyes for the coloration of synthetic fibers.



For 1 - 4: R and R' = alkyl.

2: W and X = CN, CO₂ alkyl, or SO₂ aryl.

3: Y = H, Cl, F.

4: R' = alkyl or aryl; Z = S or O.

The aldehydes required were obtained by Vilsmeier-Haack formylation of 4-(1-alkyl-2,3-dihydro-2,2-dimethyl-1H-indol-3-yl)-N,N-dialkylbenzeneamines which were readily prepared from the reaction of 2-chloroisobutyraldehyde (2-ClIBA) and aromatic amines. This reaction could be controlled to produce indoline or indole products. For example, reaction of one mole of 2-ClIBA with five moles of aniline at the reflux temperature (about 130°C at 1 atm with retention of the one mole of water produced) produced 2,2-dimethyl-3-[p-(amino)phenyl]indoline. When this reaction is heated to 190°C (by distillation of the water), 2,3-dimethylindole is produced.

These indoline or indole forming reactions were easily scaled up and worked well with substituted (*ortho*-, *meta*-, *N*-) anilines as well as with other 2-haloaldehydes such as 2-bromocyclohexanecarboxaldehyde and 2-bromodiphenylacetaldehyde. Two useful variations are as follows:

(1) reaction of equimolar quantities of *N*-methylaniline and 2-ClIBA with four moles of *N,N*-dimethylaniline to produce directly 1,2,2-trimethyl-3-(*p*-dimethylaminophenyl)indoline.

(2) reaction of equimolar quantities of *p*-toluidine and 2-ClIBA in refluxing pyridine to produce 2,3,5-trimethylindole.