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New Cyanine Dyes: Norindosquarocyanines

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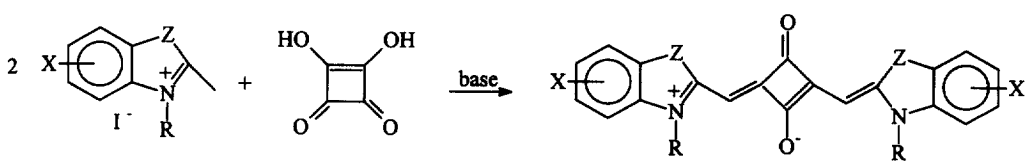
Abstract:

Synthesis of new acidochromic-based dyes is presented. The dyes obtained have acid absorbance maxima at 640-700 nm and expose spectral changes in the pH-range from 8 to 12.

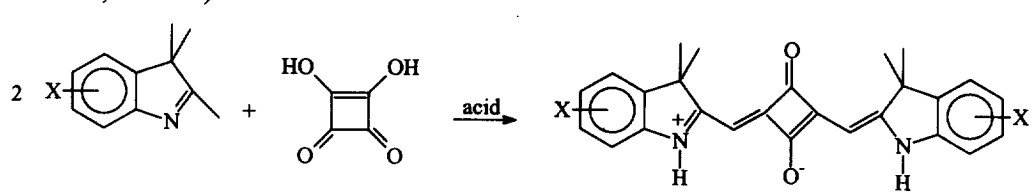
It is known that squaric acid undergoes base-catalyzed condensation with quaternary salts of certain heterocycles possessing activated methyl groups forming squarilium dyes **1**[1,2] (Scheme 1).



R = alkyl Z = S, $C(CH_3)_2$ **1**

Scheme 1

We have found that free bases of substituted 2,3,3-trimethylindolenines **2a-g** react with squaric acid under acid catalysis resulting in norindosquarilium dyes **3a-g** in high yields (Scheme 2, Table 1).[3]



2a-g **3a-g**

Scheme 2

0040-4039/99/$ - see front matter
PII: S0040-4039(99)00650-4

Table 1

Product	X	Yield (%)	λ_{max}acid (nm)	λ_{max}base (nm)	pKa
3a	H	77	649	509	11.9
3b	[4,5]benz-	80	680	535	11.6
3c	5-N_2O	80	666	581	8.3
3d	5-CH_3CONH	67	676	523	11.5
3e*	5-NH_2	32	698	518	12.0
3f	5-OH	78	679	440	11.4
3g	5-C_4H_9	45	660	515	12.6

*obtained by deacetylation of **3d** with $BF_3 \cdot CH_3OH$[4]

The protonated forms of the dyes **3a-g** have absorbance maxima close to those of alkylated analogues.[1,2] Determination of pKa values[5] was undertaken in ethanol:universal buffer (50:50) (Fig.1).

Forth-and-back experiments showed complete reversibility of spectral changes. Some of the dyes obtained can be used as pH-sensitive components of optical sensors with commercial laser diodes emitting at 680nm.

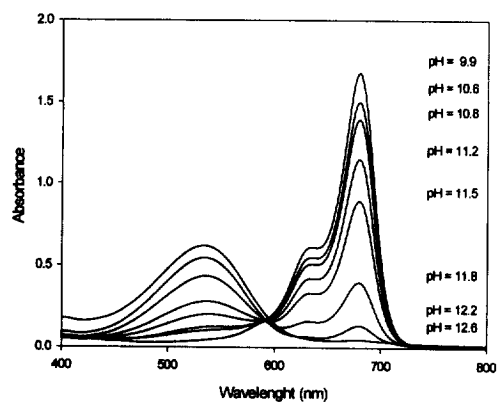


Figure 1. Absorbance spectra of the dye **3b** at indicated pH values.

Acknowledgements

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References and notes

[1] Kuramoto N, Natsukawa K, Asao K Dyes and Pigments 1989;11:21-35.

[2] Terpetschnig E, Szmacinski H, Lakowicz J.R. Analytica Chimica Acta 1993;282,633-641.

[3] Representative procedure for **3a**: 637 mg (4mmol) of 2a, 228 mg (2mmnol) of squaric acid and 500mg of p-toluenesulfonic acid monohydrate in a mixture of 20ml butanol and 10ml benzene were heated at reflux for 2h.; the water was removed azeotropically using a Dean-Stark trap. The resulting crystals were filtered out and washed with ether. Recrystallization from methanol and drying yielded 611 mg of **3a** (77%): $\varepsilon_{acid} = 1.61 \cdot 10^5$, ^{1}H-NMR (250MHz, DMSO-d^6): δ ppm, J Hz; 1.44 (s, 12H). 5.55 (s, 2H), 7.09-7.49 (m, 8H); Analysis: calculated for $C_{26}H_{24}O_2N_2$, C, 78.76; H, 6.1; N, 7.07. Found, C, 78.78; H, 5.98; N, 6.93. MALDI m/z 396.9 (M^+, 100), 397.9 (M^++H^+, 98).

[4] Sihlbom L Acta Chem. Scand. 1954;8:529-530.

[5] The average pKa are calculated using the following equation: $pKa = pH - \log [(A_{max}-A)/(A-A_{min})]$.