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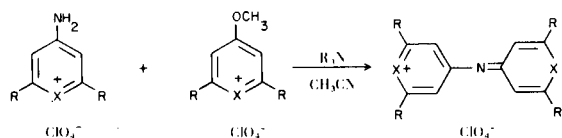
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Azapyrylocyanine and thiopyrylocyanine dyes were prepared from a 4-aminopyrylium or 4-aminothiopyrylium perchlorate and a 4-methoxyppyrylium or thiopyrylium perchlorate in the presence of a tertiary amine. The absorption spectra of these dyes was shifted 107-125 nm to shorter wavelength compared to the corresponding methine dyes.

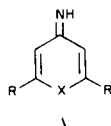
J. Heterocyclic Chem., 14, 539 (1977).

Azacyanines are cyanine dyes in which the methine group is replaced by a nitrogen atom, and examples with a variety of heterocyclic nuclei have been prepared (1). However, no examples have been reported with pyrylium groups, probably because of the difficulty encountered in obtaining suitable precursors. This paper describes the preparation of azapyrylocyanines and thiopyrylocyanines (2) and compares their absorption spectra with the corresponding methine analogs.

We recently reported a convenient general synthesis for 4-aminopyrylium salts from pyrones or flavones and activated isocyanates (3). These amines serve as suitable starting materials for the preparation of azapyrylocyanines by the following route. The yields of dyes were modest, probably due to the low order of reactivity of the imino

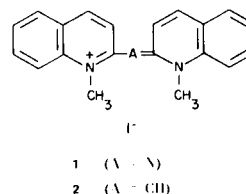


compound A which is probably an intermediate in this



reaction. Table I lists the azacyanine dyes that were prepared and their physical properties.

A comparison of the long-wavelength absorptions of azacyanine dyes with the corresponding cyanine dyes shows that the nitrogen atom causes a large hypsochromic shift. A published example of this effect reported that the aza dye **1** absorbs 99 nm shorter than the corresponding cyanine **2** (1). Since pyrylocyanine dyes show



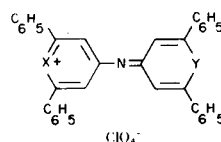
absorption at longer wavelengths than any other class of cyanine dyes, we thought it would be of interest to determine the effect of the nitrogen atom on the spectra with the hope of observing very large hypsochromic shifts. Table II lists the long-wavelength absorptions of the aza dyes and the corresponding cyanine dyes, and it is seen that the hypsochromic shifts vary from 107-125 nm.

EXPERIMENTAL

Melting points were determined in a Mel-Temp apparatus and are uncorrected. The absorption spectra were recorded on a Cary model 17 spectrometer.

Table I

Physical Properties of Azacyanines



Compound No.	X	Y	M.p., °C	Yield %	Solvent for Recrystallization	Empirical Formula	Anal. Calcd./Found		
							C	H	N
4	O	O	310 dec.	36	CH ₃ CN	C ₃₄ H ₂₄ ClNO ₆	70.7	4.2	2.4
							70.5	4.0	2.6
5	S	O	257-258	20	CH ₃ CN	C ₃₄ H ₂₄ ClNO ₅ S	68.7	4.1	2.4
							68.4	4.1	2.2
6	S	S	222-223	19	C ₂ H ₅ OH	C ₃₄ H ₂₄ ClNO ₄ S ₂	66.9	4.0	2.3

Table II

Spectra of Azacyanines and Cyanines

Compound No.	λ max ($\epsilon \times 10^{-3}$) in Acetonitrile	Corresponding Cyanine max ($\epsilon \times 10^{-3}$)
4	436 (36.0)	543 (120.0)
	345 (28.0)	379 (27.2)
	265 (38.5)	268 (26.4)
5		230 (21.6)
	460 (34.4)	585 (80.1)
	450 (31.5)	390 (21.6)
	358 (23.0)	257 (31.7)
6	257 (38.0)	238 (33.5)
	499 (51.7)	622 (113.5)
	362 (25.3)	390 (20.8)
	263 (40.0)	255 (28.7)
	197 (80.0)	242 (31.0)

4-Amino-2,6-diphenylthiopyrylium Perchlorate.

A mixture of 5.2 g. of 2,6-diphenyl-4*H*-thiopyran-4-one (4) and 2.8 g. of chlorosulfonylisocyanate was stirred until the exothermic reaction subsided, and, after chilling, the solid was collected. The solid was dissolved in 35 ml. of hot acetic acid, 3 ml. of 70% perchloric acid was added and, after cooling, the product was collected, yield 4 g. (from alcohol), m.p. 225-226°. The λ max ($\epsilon \times 10^{-3}$) in acetonitrile were 324 (30.6) and 260 nm (19.2).

Anal. Calcd. for $C_{17}H_{14}ClNO_4S$: C, 56.1; H, 3.9; N, 3.8. Found: C, 55.9; H, 4.0; N, 3.7.

General Procedure for the Preparation of Azacyanines.

A mixture of 5 mmoles of 4-amino-2,6-diphenylpyrylium or thiopyrylium perchlorate, 5 mmoles of 4-methoxy-2,6-diphenylpyrylium or thiopyrylium perchlorate and 5 mmoles of diisopropylethylamine in 50 ml. of acetonitrile was heated on a steam bath for 1/2 hour and then allowed to stand for several hours. The solid was collected, washed with alcohol and recrystallized.

An attempt to prepare 4 by refluxing 4-amino-2,6-diphenylpyrylium perchlorate and 2,6-diphenyl-4*H*-pyran-4-one in acetic anhydride gave 4-acetamido-2,6-diphenylpyrylium perchlorate, m.p. 255-256°.

Anal. Calcd. for $C_{19}H_{16}ClNO_6$: C, 58.5; H, 4.1; N, 3.6. Found: C, 58.5; H, 4.3; N, 3.6.

REFERENCES AND NOTES

- (1) F. M. Hamer in "The Chemistry of Heterocyclic Compounds", Vol. 18, "The Cyanine Dyes and Related Compounds", A. Weissberger, Ed., Interscience, New York, N. Y., 1964, Chapter XII.
- (2) This is not an accurate name for this class of compounds but is used for convenience in this paper.
- (3) J. VanAllan, G. Reynolds and S. Chang, *J. Heterocyclic Chem.*, **11**, 195 (1974)
- (4) F. Arndt, P. Nachtwey and J. Pusch, *Chem. Ber.*, **58**, 1633 (1925).