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THE ROLE OF THE "BASICITY" AND OF THE EXTRACHROMOPHORIC CONJUGATION IN THE ABSORPTION OF SYMMETRICAL TRIMETHINE CYANINES DERIVED FROM THIAZOLE NUCLEI

Alberto Gasco, Ermanno Barni and Gaetano Di Modica
Istituto Chimico della Università, Torino (Italia)

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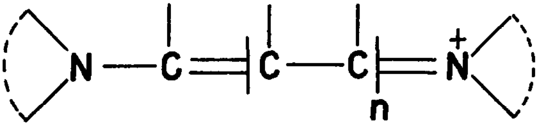
A symmetrical cyanine dye is formed by vinylene prolongation of the amidinium ion system in which nitrogen atoms form part of equal heterocyclic rings:



The qualitative explanation of the absorption of these dyes in terms of molecular structure was performed by L.G.S. Brooker and his co-workers (1,3).

According to the point of view of the Authors above the λ_{max} of a symmetrical cyanine mainly depends on three factors: 1) Length of the conjugated chain, 2) Basicity of the nuclei, 3) Extrachromophoric conjugation.

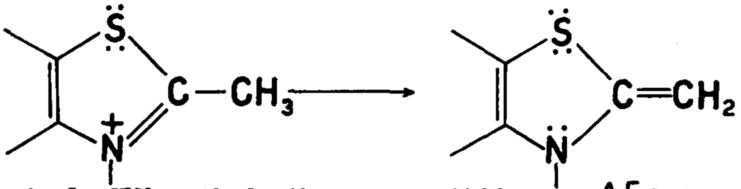
The influence of the length of the polymethine chain was studied also with the aid of quantum methods (2) but the influence of the factors 2) and 3) was investigated only qualitatively (1, 3).

In order to evaluate the relative importance of the last two factors on the position of the absorption of some symmetrical cyanines derived from the following condensed thiazole nuclei: 2-CH_3-thiazolium, 2-CH_3-benzothiazolium, 2-CH_3-naphtho[2,3-d]thiazolium, 2-CH_3-naphtho[1,2-d]thiazolium, 2-CH_3-naphtho[2,1-d]thiazolium, 2-CH_3-phenanthro[9, 10-d]thiazolium (see Table I), some correlations were performed.

The basicity of the thiazole nucleus is related, according to L.G.S. Brooker, to the loss of ring stabilization in passing from the positively charged form I to the net uncharged form II:

I II

The same loss in stabilization follows the formation of the methylene base from the corresponding cation (4):



Using a simple HMO method, the energy difference ΔE_b between quaternary salts of the 2 methyl derivatives above and their methylene bases, was calculated. The coulomb and resonance integrals used for the heteroatoms were:

$\alpha_S = \alpha+\beta$, $\alpha_{\ddot{N}} = \alpha+1{,}5\beta$, $\alpha_{\overset{+}{N}} = \alpha+2\beta$, $\beta_{C=S} = 0{,}8\beta$, $\beta_{C-\ddot{N}} = 0{,}8\beta$, $\beta_{C-\overset{+}{N}} = \beta$

The methyl group was treated as a heteroatom according to Streitwieser (5). Coulomb integrals for the carbon atoms adjacent to the heteroatoms were expressed in the following way: $\alpha_{\dot{C}} = \alpha+\delta_C \cdot \beta$ where $\delta_C = 0{,}1\sum\delta_X$. In particular, for the methyl group treated as a heteroatom, a value of $\delta_{C-CH_3} = -0{,}2$ was used. The substituent effects of the N-alkyl group were disregarded. The results of these calculations and the Δ values of the deviations (3) for the nuclei considered are reported in Table I.

A plot of ΔE_b values versus Δ values is reported in Fig. 1. The satisfactory linear correlation between these sets of data is clear. It is interesting to note that, with the aid of the quantum methods also, the appreciably larger deviation of the 2-CH_3-naphtho[1,2-d]thiazolium than the 2-CH_3-naphtho[2,1-d]thiazolium (3) is not entirely explained.

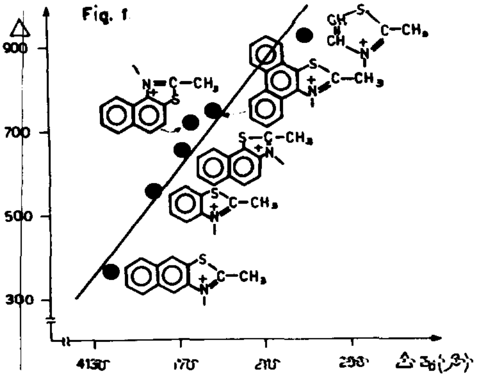


Fig. 1

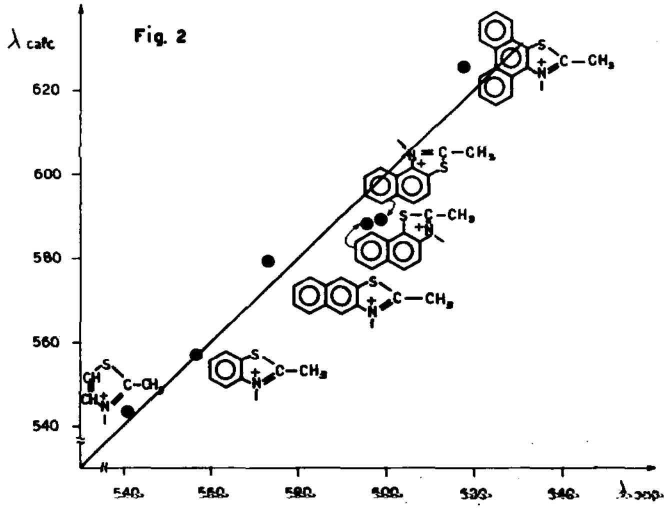
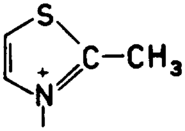
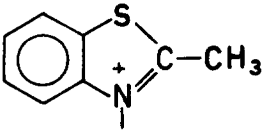
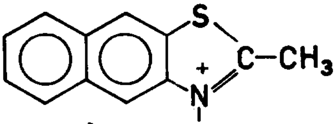
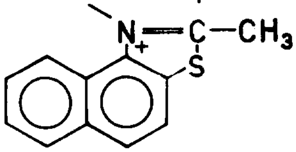
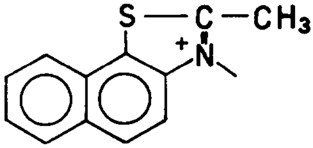
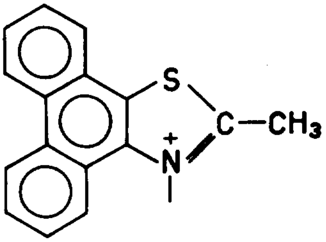


Fig. 2

TABLE I

COMPOUNDS	ΔE_b [1]	Δ [2]	ΔE_r [3]	λ_{max} $\hat{\nu}$ [4]	λ_{max} $\hat{\nu}$ [5]
	4.2289	925	1.7366	541.0 18484	543.5 18399
	4.1592	555	3.5947	556.5 17969	557.1 17949
	4.1379	365	5.2494	573.0 17452	579.2 17266
	4.1759	720	5.3094	599.0 16694	589.1 16975
	4.1724	650	5.3110	595.5 16792	588.3 16998
	4.1872	745	7.1002	617.5 16194	625.0 15999

1) Loss of the energy (β) in passing from the cation to the corresponding methylene base.

2) Deviation; values taken from reference. (3)

3) Resonance energy ($-\beta$)

4) λ_{max} (mμ) in $MeNO_2$ of the principal absorption of the symmetrical trimethinecyanine $\hat{\nu}$ = wave number (cm-1) Values taken from reference. (3)

5) λ_{max} and $\hat{\nu}$ calculated from equation (1).

The extension of the scope of the possible charge migration in the dye ion to carbon atoms of the rings lying beyond nitrogen atoms is called by L.G.S. Brooker extrachromophoric conjugation (1).

It appears reasonable to suppose that, for the nuclei of Table I, the extension of charge migration is proportional to the delocalization energy. The calculated delocalization energies are reported in Table I (ΔE_r values). If now $\hat{\nu}$ (see Table I) of the first absorption peak of trimethine symmetrical dyes derived from the reported quaternary salts is considered as a linear combination of ΔE_b and ΔE_r i.e. $\hat{\nu} = a + b\,\Delta E_b + c\,\Delta E_r$ a rather positive regression surface is obtained. The values of a, b and c were calculated with the usual methods (6) giving $\hat{\nu} = 48398 - 6888\,\Delta E_b - 501\,\Delta E_r$ (R = 0.972) 1). The λ_{max} calculated from equation 1) are satisfactorily in agreement with experimental λ_{max} values (see Table I and Fig. 2).

It can be deduced from equation 1) that the susceptibility of $\hat{\nu}$ to the extrachromophoric conjugation and to the "basicity" are in the ratio 1:10.

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