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Near-infrared Absorbing Polymethine Dyes Terminally Substituted by 1-Benzothiopyrylium Ring

Hiroyuki NAKAZUMI,* Shigeru WATANABE, Seiji KADO, and Teijiro KITAO
Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591

Unsymmetrical polymethine near-infrared dyes terminally containing 1-benzothiopyrylium ring and ***N,N***-dimethylamino group were first prepared from 2-methyl-, 4-methyl-, and 2,4-dimethyl-1-benzothiopyrylium salts. It is found that the maximum wavelength of these dyes on PMMA is remarkably shifted to a shorter wavelength (60-200 nm) compared with that in solution.

Near-infrared absorbing dyes have become more important as the use of semiconductor laser having oscillation wavelengths in 780-830 nm which has grown in practical system, both for reading and writing of the information.$^{1)}$

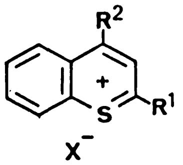
In the research on functional dyes and organic photoconductors 4*H*-thiopyran-4-one 1,1-dioxides$^{2)}$ and 4*H*-1-benzothiopyran-4-one 1,1-dioxides$^{3)}$ have been of interest as a new class of electron acceptor. However, absorption maxima of dyes with those heterocyclic group, as an acceptor, lie in the visible region.

In order to provide near-infrared absorbing dyes in a series of 1-benzothiopyran system, we selected 1-benzothiopyrylium ring as a powerful electron-acceptor and prepared new polymethine dyes in good yields by condensation of methyl or dimethyl 1-benzothiopyrylium salts with vinylogous aromatic aldehydes. Few benzothiopyrylium styryl dyes having absorption bands beyond 750 nm have so far been reported.$^{4)}$

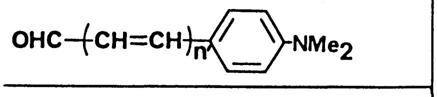
4-Hydroxy-2-methyl-1-benzothiopyrylium perchlorate 1a (mp 184.3 °C), which was conveniently prepared by reaction of 2-methyl-4*H*-1-benzothiopyran (2-methylthiochromone) with 60% perchloric acid in acetic acid, was condensed with ***p***-(dimethylamino)benzaldehyde 4a to give the styryl dye 5a in 85% yield. The 4-phenyl and 4-ethoxy derivatives 5b and 5c were similarly obtained from 1-benzothiopyrylium salts 1b$^{5)}$ and 1c (mp 158.1 °C),$^{6)}$ respectively.

Though the absorption maxima of these styryl dyes were below 700 nm, these were more strongly bathochromic (ca. 100 nm) than the corresponding heteroanalogous nitrogen compounds. Similar results have been observed in terminally sulfur-containing cyanine dyes.$^{7)}$

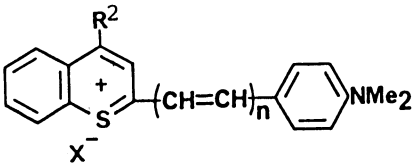
Further pronounced bathochromic shift in the chromophoric system was attainable by increasing of the conjugated chain by vinyl groups (6c and 7c). Additional bathochromic shift was observed by replacement of the 4-hydroxy or 4-ethoxy group in 5a or 5c, by phenyl group (5b). Compound 6b shows an absorption band beyond 750 nm.



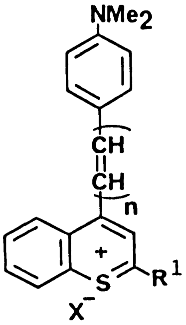
1a: R^1=Me, R^2=OH, X=ClO_4
1b: R^1=Me, R^2=Ph, X=ClO_4
1c: R^1=Me, R^2=OEt, X=BF_4
2a: R^1=Ph, R^2=Me, X=ClO_4
2b: R^1=OEt, R^2=Me, X=BF_4
3: R^1=Me, R^2=Me, X=ClO_4



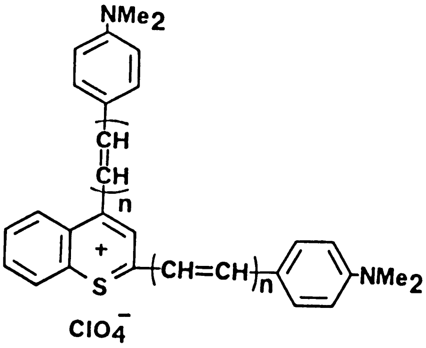
4a: n'=0
4b: n'=1
4c: n'=2



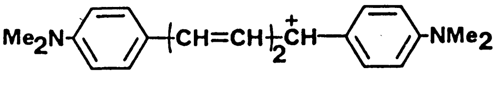
5a: R^2=OH, X=ClO_4, n=1
5b: R^2=Ph, X=ClO_4, n=1
5c: R^2=OEt, X=BF_4, n=1
6b: R^2=Ph, X=ClO_4, n=2
6c: R^2=OEt, X=BF_4, n=2
7c: R^2=OEt, X=BF_4, n=3



8a: R^1=Ph, X=ClO_4, n=1
9a: R^1=Ph, X=ClO_4, n=2
10a: R^1=Ph, X=ClO_4, n=3



11: n=1
12: n=2



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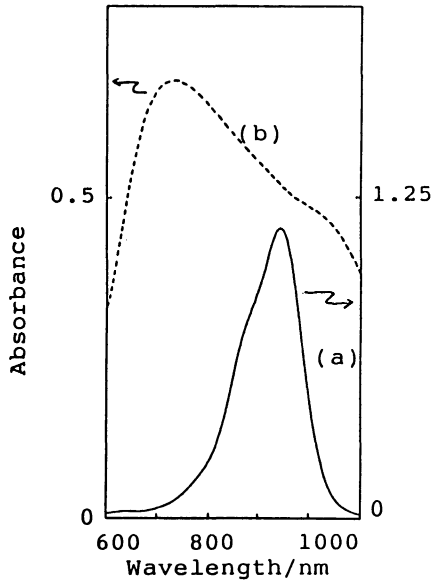

Fig. 1. Absorption spectra of 10a in 1,1,2,2-tetrachloroethane (a) (1×10^{-5} mol dm^{-3}) and on PMMA (b) (thickness: 70 nm).

Table 1. Absorption maxima and solubilities of polymethine dyes 5-12[a)]

Dye	Yield/%[b)]	λmax/nm (εx10^{-4})[c)]	Solubility/wt%[d)]
5a	85	662 (8.74)	-
5b	78	711 (5.47)	16.1
5c[e)]	51	664 (8.33)	4.60
6b	91	807 (3.96)	5.78
6c	63	748 (9.10)	4.35
7c	81	833 (7.66)	2.59
8a[f)]	93	738 (11.3)	0.86
9a	96	842 (14.8)	0.12
10a	92	944 (11.8)	4.92
11	79	836 (10.3), 640 (4.62)	6.41
12	75	954 (9.14), 715 (3.93)	4.24

a) All new compounds gave satisfactory spectral and analytical data. b) Isolated yields. c) Measured in 1,1,2,2-tetrachloroethane. d) Solubility of the polymethine dye was determined in 1,1,2,2-tetrachloroethane at 20 °C. e) Ref. 5. f) Ref. 4.

Although empirical relationships in cyanine dyes suggest that further vinylene shift could be achieved by increasing of polymethine chain, synthetic problems of vinylogous aromatic aldehyde are considerable.

An alternative approach to polymethine dye absorbing beyond 750 nm is to make use of the double bond in the terminal heterocyclic ring by 4-substitution instead of 2-substitution of the terminal benzothiopyrylium ring. Thus, 2-phenyl-4-methyl-1-benzothiopyrylium salt 2a (mp 158.7 °C)[8)] which was prepared by methylation of thioflavone with methylmagnesium iodide was condensed with vinylogous aromatic aldehyde 4a-4c to give polymethine dyes 8a,[4)] 9a, and 10a. The bathochromic effect (ca. 30-40 nm) of the double bond in the terminal benzothiopyrylium ring can be seen by comparing 8a and 9a with the corresponding 5b and 6b, respectively. The intense absorption maxima of polymethine dyes 9a and 10a are displaced to 842 nm and 944 nm, respectively, by this effect.

However, when 2-ethoxy-4-methyl-1-benzothiopyrylium salt 2b, obtained by O-ethylation of 4-methyl-2*H*-1-benzothiopyran-2-one with triethyloxonium tetrafluoroborate, was used as a starting 1-benzothiopyrylium salt, the mixture[9)] of a styryl dye and a dimmer of the starting material 2b was obtained and could not be separated.

2,4-Dimethyl-1-benzothiopyrylium salt 3 (mp 128.3 °C) which was a starting 1-benzothiopyrylium salt with two active methyl groups, was easily prepared by methylation of 2-methylthiochromone with methylmagnesium iodide. The dyes 11 and 12 with branched polymethine chain, which can be viewed as examples of diphenylmethane dye vinylogues, could be obtained by condensation of 3 with excess aromatic aldehydes 4a and 4b, respectively, in reflux of ethanol. These dyes are not unsymmetrical polymethine chromophore, but symmetrical cyanine chromophore having cyclic π-fragments on the central of polymethine chain. The absorption maximum of 11 shows the shift (ca. 20 nm in acetic acid) to longer wavelength by the effect of coupling of polymethines with cyclic *π*-fragments, comparing with 13.

These dyes proved to give the donor-acceptor chromophore having absorption maxima in the near-infrared region in combination of 1-benzothiopyrylium ring and ***N,N***-dimethylamino polymethine residue.

For use in a DRAW disk polymethine dyes need to have an absorption band in 750-800 nm, as the maximum wavelength of cyanine dyes on a substrate in a DRAW disk is slightly shifted to a longer wavelength (20-30 nm) compared with that in solution.[1)]

On the other hand, new polymethine dye 10a undergoes pronounced hypsochromic shift on passing from 1,1,2,2-tetrachloroethane (944 nm) to poly(methylmethacylate) (735 nm), as shown in Fig. 1. This pronounced shifts in other polymethine dyes prepared were observed (ca. 60-100 nm) and may arise from H-aggregates of dyes which cause an hypsochromically shifted color band in cationic polymethine dyes.[7)]

Thus, those polymethine dyes should have absorption band at 880-990 nm in 1,1,2,2-tetrachloroethane in order to use as organic colorants for the optical data storage, because of this pronounced hypsochromic shift on PMMA. From this reason, dyes 10a and 12 can be selected as the absorber for optical disk memory system, and also have sufficient solubility for formation of thin layer by spin-coating technique, as shown in Table 1. Compound 11 is also possible as an absorber, due to broadening of its absorption maximum and good solubility.

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8) The mp was determined by means of DSC.
9) Absorption maxima of styryl dye 8b (R^1=OEt, X=BF_4, n=1) and a dimer show at 681 and 596 nm, respectively, as an inseparable mixture.

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