Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 74 (2007) 744–748

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Short communication

Approximation of basicity and absorption region in large arrays of polymethine dyes with heterocyclic end groups

M.L. Dekhtyar*

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya 5, 02094 Kiev-94, Ukraine

Received 20 March 2006; accepted 26 March 2006
Available online 16 May 2006

Abstract

For a large array of polymethine dyes (about 80 carbocyanines with various end nuclei), effective topological parameters of the long-chain approximation (electron donor ability F and effective length L) are calculated and correlated with experimental chemical and spectral dye characteristics (pK_a and first electronic transition wavelength).

Keywords: Polymethine dyes; Heterocyclic end groups; Long-chain approximation; End-group topological parameters; Correlation equations

Purposeful design of polymethine dyes (PMDs) calls for a method to estimate the significant properties of new structures of their heterocyclic end groups (EGs). This task implies determination of some theoretical (quantum chemical or empirical) parameters for a large number of both known and novel heterocyclic nuclei, and establishment of quantitative relationships between such parameters and experimental PMD characteristics. At the primary stage, it is expedient to apply sufficiently simple approaches which can rapidly riddle massive arrays of structures like a coarse sieve so as to select the most promising EGs and to catch the major trends in their effect on dye's chemical and spectral behaviour. The estimates thus obtained for selected interesting structures should of course be refined by a high-level (time-consuming) computational method but sometimes a significant gain in accuracy is possible even in the framework of the same (simplistic) approach, as reported in this study. The present work covers a large array of PMDs (over 80 symmetric carbocyanines $[\mathrm{EG{=}CH{-}CH{=}CH{-}EG}]^+$ with various EGs) for which we have calculated effective topological parameters of the long-chain approximation (LCA), electron donor ability F and effective length L [1–5], and correlated them with the experimentally measured [6,7] chemical and spectral PMD properties, viz., basicity thermodynamically represented by the negative logarithm of the conjugated acid dissociation constant, pK_a, and first electronic transition wavelength, λ_{exp}.

Electron donor ability and effective length, respectively, characterize EG contributions to the positions of PMD frontier levels relative to the Fermi level (an intensive index remaining practically constant within a vinylogous PMD series) and to the energy gap width (an extensive index changing in going from lower to higher vinylogues) [1–5]. The parameters F and L are additive quantities specified only by the constitution of two EGs in the topological approximation and expressed in terms of the relevant elements of the EG inverse topological matrices (Green's functions $g_j(z)$ of the energy variable z at $z = 0$) [3,4]:

$$F = \left\{ \sum_{j=1}^{2} F_j \right\}; \; F_j = \pi^{-1} \operatorname{arcctg} \left[g_j(0) \right]^{-1} \tag{1}$$

$$L = \sum_{j=1}^{2} L_j; \; L_j = -\left[2g_j'(0) + g_j^2(0) \right] \Big/ \left[1 + g_j^2(0) \right], \tag{2}$$

---

* Tel./fax: +380 44 573 26 43.
E-mail address: vrozen@mail.kar.net

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.03.019

where {…} designates taking fractional part of a number. The wavelengths in the first absorption maxima were calculated as $\lambda_{\mathrm{th}} = (L + n + 1)V$, where n is the number of vinylene groups in a PMD molecule and $V \approx 100$ nm is the empirically determined "vinylene shift" [1].

For 35 EGs of the thiazole series (see Appendix 1), the correlation equation relating basicity to F was derived: $\mathrm{p}K_{\mathrm{a}} = 47.07F - 38.87$ (the correlation coefficient $R = 0.91$). It shows excellent agreement with the previously reported correlation for a set of aza heterocyclic residues [8,9], which suggests a rather stable regularity. Small mean-square variance between experimental and calculated data $\tilde{\delta}$ (0.91 pK_{a} units) points to high reliability of the estimates based on the dependence found.

For 51 EGs of the thiazole series (see Appendix 1), the following correlation was found between the experimental and topology-based values for the longest absorption wavelength: $\lambda_{\mathrm{exp}} = 0.29\lambda_{\mathrm{th}} + 453.32$ ($R = 0.89$). The value of $\tilde{\delta}$, however, amounts to 126.01 nm and so a large error makes questionable the very possibility to directly apply the LCA method in practically oriented estimations of absorption wavelengths. This variance is hugely contributed by the so-called systematic error of the calculation which arises from the neglect of interelectronic interaction in the framework of LCA (as in any Hueckel-type model). Here we suggest a straightforward method to eliminate the systematic error using the available experimental data of the sample concerned. To this end, one should calculate the corrected values of effective length, $L_{\mathrm{corr}} = aL + (a - 1)n + b/V$, which are dictated not only by the starting theoretical parameter L but also by the parameters of the correlation equation $\lambda_{\mathrm{exp}} = a\lambda_{\mathrm{th}} + b$. The accordingly corrected values λ_{corr} (calculated by L_{corr} analogously to λ_{th}) reproduce experimental data much more accurately: $\tilde{\delta}$ decreases to 17.60 nm (less than one-seventh of the initial value). An important advantage of the technique developed is that the numerical parameters of the correlation equation found for a sufficiently large EG sample can be used to correct the effective lengths of arbitrary heterocyclic residues (not only those within the sample under consideration). This feature arises from the fact that the values L_{corr} obtained for any array implicitly take into account the general effects of interelectronic interaction. For instance, the correlation equation parameters for the array of 51 EGs of the thiazole series were applied to correct the effective lengths in another miscellaneous array which included 31 aza, thiaza, and oxa heterocyclic residues (see Appendix 2); as a result, the value $\tilde{\delta}$ in the latter sample was reduced from 98.11 to 34.20 nm.

The correlation analysis performed demonstrates that PMD molecular indices of intensive character (basicity) can be estimated better than those of extensive character (first electronic transition wavelength). At the same time, the suggested procedure for correcting the values of L affords a significantly increased (by not less than half an order) accuracy for λ_{exp} estimation and may therefore improve the prediction quality for other PMD properties associated with absorption region (e.g., linear and nonlinear polarizabilities).

Acknowledgements

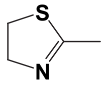
The author is thankful to the late Professor E.B. Lifshits for initiating this study and giving an access to the database of PMD experimental characteristics. Helpful discussions of the calculation methods with Professor V.M. Rozenbaum and Dr. M.N. Ushomirskii are also acknowledged.

Appendix 1. Heterocyclic nuclei of the thiazole series and their characteristics involved in the correlation analysis

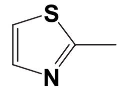
The linear approximations of basicity and absorption wavelength based on the topological parameters are shown diagrammatically for the dye end nuclei of the thiazole series. The calculated values, p$K_{\mathrm{a_{th}}}$, λ_{th}, and λ_{corr}, are indicated in the left column and the corresponding measured characteristics, p$K_{\mathrm{a_{exp}}}$ and λ_{exp}, in the right column below the corresponding structure (see the pattern). Unavailable values are designated by dashes. The Coulomb, α_{X}, and the resonance, $\beta_{\mathrm{XX'}}$, integrals for atoms and bonds are defined, respectively, as $\alpha_{\mathrm{C}} + h_{\mathrm{X}}\beta_{\mathrm{CC}}$ and $\eta_{\mathrm{XX'}}\beta_{\mathrm{CC}}$ with the commonly used h_{X} and $\eta_{\mathrm{XX'}}$ values: $h_{\mathrm{C}} = 0$, $h_{\mathrm{N}} = 1$, $h_{\mathrm{S}} = 0.7$, $h_{\mathrm{Se}} = 0.5$; $\eta_{\mathrm{CC}} = \eta_{\mathrm{CN}} = 1$, $\eta_{\mathrm{CS}} = 0.4$, $\eta_{\mathrm{CSe}} = 0.2$.

pKa_{th} pKa_{exp}

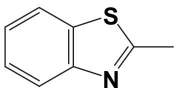
λ_{th}; λ_{corr}, nm λ_{exp}(EtOH), nm



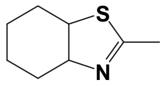
−2.00 −0.70
346; – 444



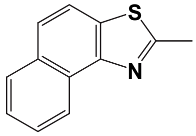
−2.00 2.40
481; 592 546



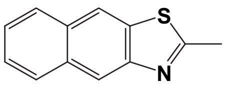
−0.43 −0.60
428; 577 559

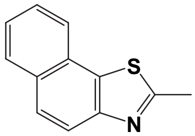


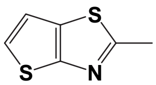
−2.00 −0.80
346; – –



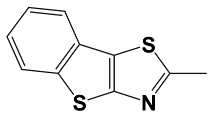
0.35 −0.04
478; 592 595

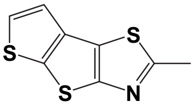

–0.96 –0.30
433; 579 570

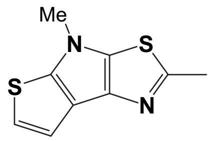

0.35 –0.40
453; 584 593

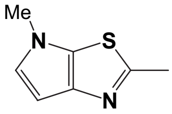

2.18 0.80
556; 614 594

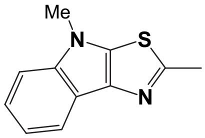

2.18 0.80
498; 597 582

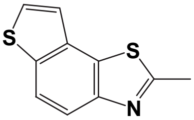

1.66 –0.14
541; 610 625

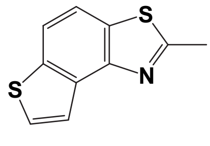

1.66 7.60
584; 622 618

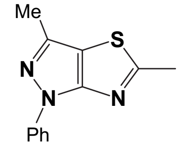

3.75 4.20
555; 614 616

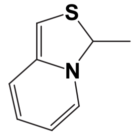

2.97 3.50
504; – –

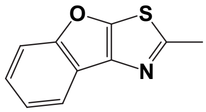

– –
587; 623 632


3.75 0.56
442; 581 584

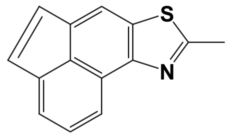

0.09 –0.32
465; 588 595

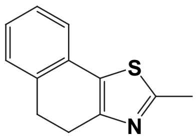

– –
446; 582 585

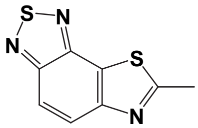

7.67 7.70
1036; – –

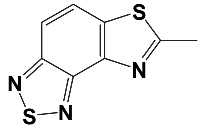

– –
527; 603 608

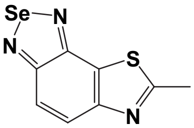

– –
515; 602 575

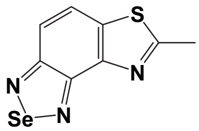

– –
516; 602 600

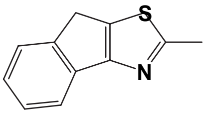

1.66 2.50
547; 611 633

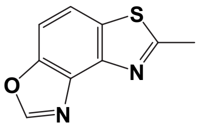

– –
460; 586 600

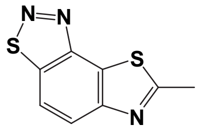

– –
478; 592 596

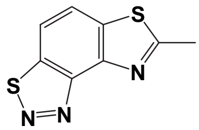

– –
471; 589 618

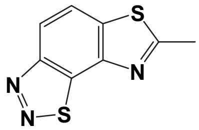

– –
478; 592 606

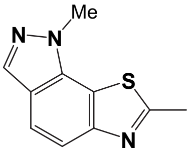

– –
490; 595 562

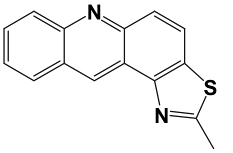

– –
452; 584 578

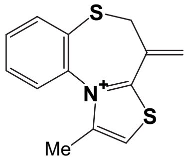

–0.17 –1.30
433; 579 570

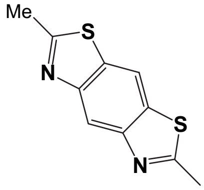

– –
584; 622 592

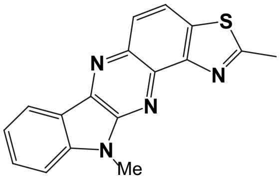

– –
449; 583 577

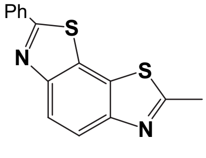

– –
457; 585 590

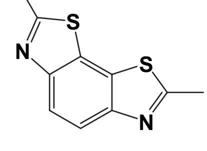

–0.96 –0.32
512; 601 610

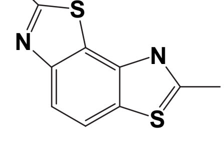

2.18 2.60
661; – 582

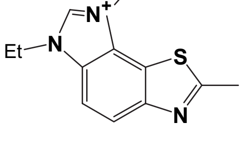

– –
434; 579 574

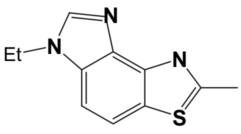

–0.17 0.50
497; 497 600


– –
456; 585 599

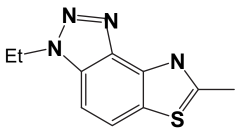

– –
448; 583 585


– –
444; 582 588

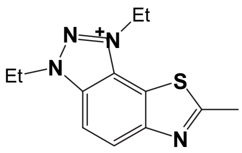

–0.17 –0.60
449; 583 576



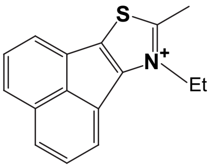
– –
462; 587 594



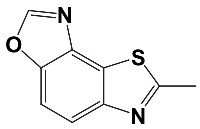
0.35 –0.6
472; 590 593



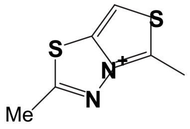
0.35 –0.6
447; 583 582



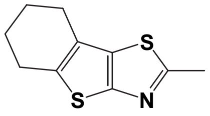
1.66 3.40
553; – 670



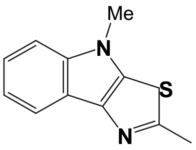
– –
436; 579 574



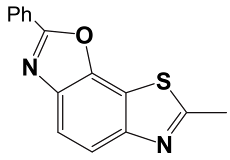
4.27 4.60
663; – 546



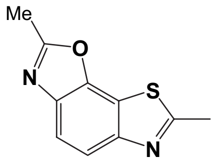
2.18 1.17
556; 614 614



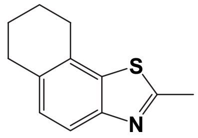
– –
587; 623 634



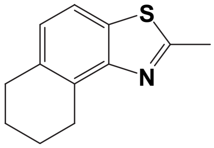
– –
450; 583 591



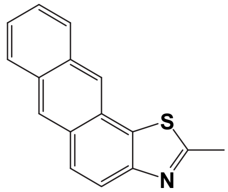
– –
444; 582 576



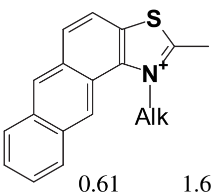
–0.43 –0.40
428; 577 573



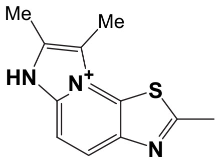
–0.43 –0.50
428; 577 571



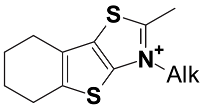
0.61 –0.20
482; 593 622



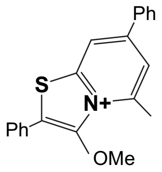
0.61 1.6
520; 604 623



0.88 0.31
467; 588 593



2.18 2.60
556; 614 614

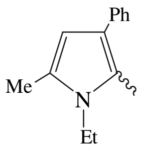


6.11 6.3
494; – 705

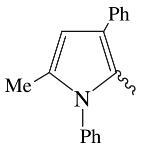
Appendix 2. Miscellaneous array of heterocyclic nuclei and their experimentally measured and theoretically estimated longest absorption wavelengths

The primary estimates, λ_{th}, the corrected values λ_{corr}, and the observed absorption wavelengths, λ_{exp}, are shown on the pattern below. The calculation was performed with $h_O = 2$; $\eta_{CO} = 0.8$ (for other atom and bond parameters, see Appendix 1).

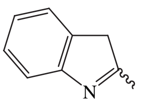
λ_{th}; λ_{corr}, nm λ_{exp} (EtOH), nm



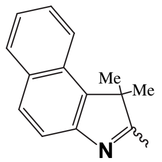
470; 589 590



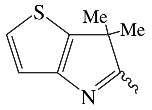
425; 576 608



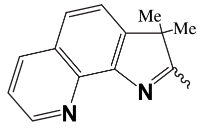
425; 576 546



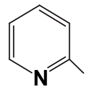
439;580 588



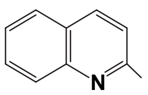
468; 589 567



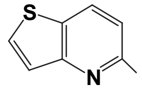
472; 590 584



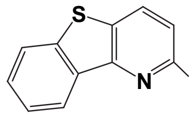
371; 561 560



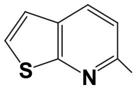
423; 576 605



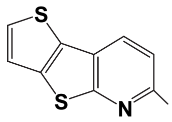
387; 565 616



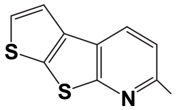
391; 566 662



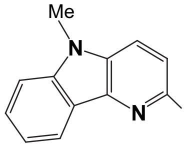
415; 573 634



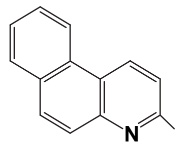
448; 583 656



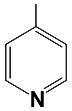
416; 574 644



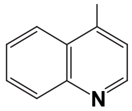
418; 574 678



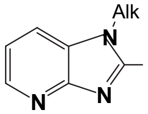
411; 572 635



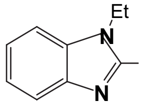
371; 561 606



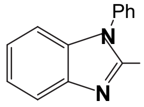
478; 591 711



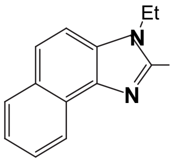
388; 565 514



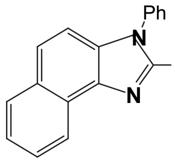
371; 561 498



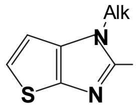
406; 571 508



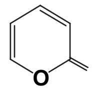
403; 570 520



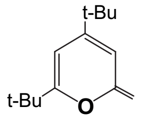
439; 580 529



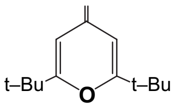
450; 583 528



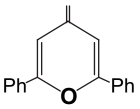
500; 597 676



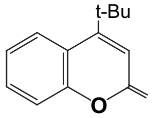
500; 598 720



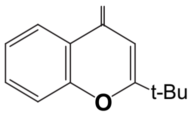
500; 598 607



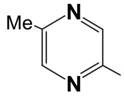
614; 631 686



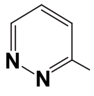
574; 619 682



597; 626 664



430; 578 618



370; 560 526

References

[1] Dyadyusha GG, Kachkovskii AD. J Inf Rec Mater 1985;13:95.

[2] Dyadyusha GG, Ushomirskii MN. Teoret Eksperim Khim 1985;21:268 [Theor Exp Chem 1985;21:257].

[3] Dyadyusha GG, Rozenbaum VM, Dekhtyar ML. Sov Phys JETP 1991;73:581.

[4] Dekhtyar ML. Dyes Pigments 1995;28:261.

[5] Dekhtyar M, Rozenbaum V, Lin S-H. MATCH Commun Math Comput Chem 2003;47:71.

[6] Lifshits EB, Ushomirskii MN, Raikhina RD, Kurkina LG. In: Proceedings of the 6th symposium on physics and chemistry of polymethine dyes. Moscow; 1996. p. 117.

[7] Lifshits EB. In: Proceedings of the 7th symposium on physics and chemistry of polymethine dyes. Moscow; 1999. p. 9.

[8 Lifshits EB, Karpova YuM, Ushomirskii MN. Khim Geterotsikl Soed 1989:1278.

[9] Lifshits EB, Raikhina RD, Kurkina LG, Ushomirskii MN. Zh Nauch Prikl Fotogr 1996;41:43.