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STRUCTURE-AFFINITY RELATIONSHIPS BY THE MTD METHOD FOR BINDING TO CELLULOSE FIBRE OF SOME HETEROCYCLIC MONOAZO DYES

Simona Timofei,*[a] Ludovic Kurunczi[a] and Zeno Simon[b]
[a] Institute of Chemistry, Romanian Academy, Bul. Mihai Viteazul 24, 1900 Timisoara, Romania
[b] Western University of Timisoara, Faculty of Chemistry-Biology-Geography, Str. Pestalozzi Nr. 16, 1900 Timisoara, Romania

Abstract. A QSAR study is performed for the modeling of the dye-textile fibre interactions, for a series of 21 heterocyclic monoazo dyes. The MTD calculations were carried out for planar structure of the dye molecules. For each dye molecule two planar conformations were considered. Good correlation results with the dye affinities (r = 0.884; s = 2.41) were obtained. The cross validation-like procedure (r^2_{cv} = 0.649) indicates a good predictability of the proposed model. Dye binding to cellulose fibre was observed in regions along the dye molecule axis.

INTRODUCTION

Theoretical studies on the mechanism of textile dye adsorption on fibres are known since the end of the 19th century. There is no unitary theory of dyeing [1]. The known models describe especially the limit cases which reflect only partially the practical processes because of the difficulties in obtaining quantitative data.

* Corresponding author. E-mail: timofei@acad-tim.utt.ro

The textile industry had to confront the more and more severe legislation of environmental protection and was obliged to stimulate also research of tinctorial dye properties.

Similarity between ligand-biological receptor interactions and dye-textile fibre interactions is considered. The arguments for the application of the QSAR techniques to the dye adsorption by fibres are derived either from the existence of thermodynamic and kinetic models of dyeing, which until now were not studied at molecular level, or from the complexity of cellulose fibre structure.

Several classical and three-dimensional QSAR methods have been applied in dye binding to cellulose [2,3,4]. Among them, the MTD (Minimal Steric Difference) method was successfully applied to the adsorption of several series of anthraquinone vat, monoazo and disperse dyes on cellulose [5-11]. The obtained results were compared with other methods and information related to the visualization of the cellulose fibre site. In previous QSAR studies [5,8,11] the MTD method was applied to a series of 49 anthraquinone vat dyes, for the modeling of dye-fibre interactions. The correlational equations with the MTD parameter (r^2 values between 0.903 and 0.941) and the cross validation-like procedure (r^2_{CV} values in the range of 0.827–0.878) indicated good correlation with dye affinity and with prediction results. A comparison between Free-Wilson and MTD results was performed, also, for a series of disperse azo dyes, which were applied to cellulose fibre [6].

This paper presents the application of the MTD method to the binding to cellulose of some heterocyclic azo dyes, considered planar in a first approximation. The dye structure and experimental affinities are presented in table 1.

METHODS

Experimental Affinities

The dye affinity expresses the driving dyeing force and an analogy with biological activity is considered. The experimental dye affinity values of the 21 heterocyclic monoazo dyes have been taken from reference [12] for compounds 1, 4, 8, 9; reference [13] for compounds 6, 7, 11, 12, 14-21; reference [14] for compounds 2, 3, 5, 10, 13.

MTD Method

The minimal steric difference (MTD) parameter [15] is considered as a measure of steric misfit between the dye molecules and the 'receptor site' on the cellulose fibre. The hypermolecule resulted from the MTD method can be considered a topological network representing the fibre receptor and it is obtained by approximate (non hydrogen) atom per atom superposition of the whole set of molecules M_i = 1, 2,..., N. The resulted vertices j = 1, 2,..., M of the hypermolecule correspond to the positions of these atoms. If molecule M_i occupies the vertex j, x_{ij} = 1 and x_{ij} = 0 if this vertex is not occupied. The minimal steric difference MTD of the molecule i with respect to the receptor is calculated by the equation:

$$MTD_i = s + \sum_j \varepsilon_j \cdot x_{ij} \qquad (1)$$

with ε_j = −1, 0 or +1 for the vertices attributed to the receptor cavity, exterior vertices or receptor walls, and s-the total number of cavity vertices. The procedure is started with an initial set of ε_j attribution, which contains the user's "chemical intuition" about the quality of the vertices. If a molecule can adopt several low energy conformations (or can be superposed in several ways in the hypermolecule), in the binding site it will adopt the one that fits best into the receptor (i.e., with the lowest MTD value) [15].

During the MTD method sometimes the obtained binding site can be fragmented. In such situations the MTD-CONNEX variant is applied, when beneficial vertices in the optimization procedure form a connected topological network [16].

The 'leave-one-out' [17] cross-validation procedure was used in order to validate the proposed models. MTD calculations have been carried out by a program developed from reference [15] at the Institute of Chemistry of Timisoara.

RESULTS AND DISCUSSIONS

In the hypermolecule construction two planar isomers for each compound were considered. They were obtained by the rotation of the coupling component around the bond between the azo nitrogen atom and the aromatic carbon atom of the coupling component.

The start hypermolecule was built up by imposing chemical criteria:

$$S^{o}\begin{cases} j(\varepsilon=-1):9,10,11,12,13 \\ j(\varepsilon=0):1-8,14-21,30-44 \\ j(\varepsilon=+1):23-27 \end{cases}$$

In a first step the atom connectivity was not considered in the hypermolecule construction. Through an optimization procedure based on the regressional coefficient as statistical test [15], following optimized map and regressional equation was obtained:

$$S_I^{*}\begin{cases} j(\varepsilon=-1):5,10-13 \\ j(\varepsilon=0):1-4,6-8,14,17-19,28-44 \\ j(\varepsilon=+1):9,15,16,20-27 \end{cases}$$

$$\hat{A}_I = 21.55(\pm 1.52) - 2.38(\pm 0.28)MTD_I \qquad (2)$$
$$r = 0.891 \quad s = 2.33 \quad F = 73.25 \quad r^2_{CV} = 0.691$$

The optimized receptor map is presented in figure 1.

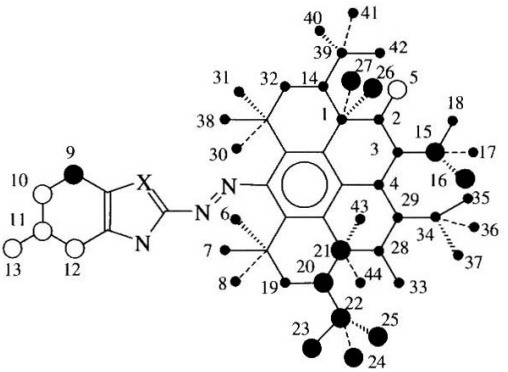


FIGURE 1. Non-connected hypermolecule and vertex numbering for the heterocyclic monoazo dyes. Beneficial vertices ($\varepsilon_j = -1$) are marked by open circles, detrimental vertices ($\varepsilon_j = +1$) by black filled circles, irrelevant vertices ($\varepsilon_j = 0$) by dots.

When molecular connectivity was considered, starting with the same start hypermolecule following equation and optimized receptor map (see figure 2) was obtained:

$$S_2^* \begin{cases} j(\varepsilon = -1): 11-13,38 \\ j(\varepsilon = 0): 1,3-8,10,14-19,21,28-37,39-44 \\ j(\varepsilon = +1): 2,9,20,22-27,34 \end{cases}$$

$$\hat{A}_2 = 22.82(\pm 1.72) - 3.54(\pm 0.43)MTD_2 \qquad (3)$$
$$r = 0.884 \quad s = 2.41 \quad F = 67.79 \quad r^2_{CV} = 0.649$$

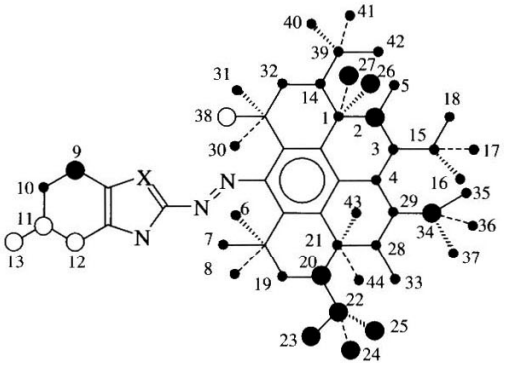
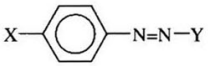


FIGURE 2. Connected hypermolecule and vertex numbering for the heterocyclic monoazo dyes. Beneficial vertices (ε_j = -1) are marked by open circles, detrimental vertices (ε_j = +1) by black filled circles, irrelevant vertices (ε_j = 0) by dots.

MTD results are presented in Tables 1 and 2. Statistical results suggest a good correlation with the dye affinity and a good predictability for the proposed MTD model.

The optimized receptor map indicates in both situations (in the absence and presence of molecular connectivity) similar predictions. Thus, the presence of benefic vertices along the dye molecular axis and addition of condensed aromatic nucleus in the heterocyclic dye moiety are favorable for dye-fibre interactions.

TABLE 1. Experimental affinities (A) and MTD results for the heterocyclic azo dyes*



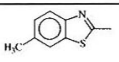
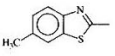
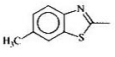
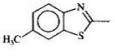
No	X	Y	A (kJ/mole)	j for x_{ij} = 1	MTD_0	MTD_1	$Á_1$	MTD_2	$Á_2$
0	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
1a		γ	22.26	1-13	0	1	19.17	-	-
1b		γ	22.26	4, 9-13, 21, 28-31, 33, 38	0	-	-	1	19.73
2a		γb	15.69	1-12	1	2	16.79	-	-
2b		γb	15.69	4,9-12,21, 28-31, 33, 38	1	-	-	2	15.74
3a		γa	14.35	6, 9-12, 19-25	1	-	-	-	-
3b		γa	14.35	1, 9-12, 14, 32, 38-42	1	3	14.41	2	15.74
4a		H	14.48	1-18	0	4	12.04	3	12.19
4b		H	14.48	4, 9-13, 20, 21, 28-31, 34-38	0	4	12.04	3	12.19
5a		H	13.56	1-18	1	5	9.66	4	8.64
5b		H	13.56	4, 9-12, 20, 21, 28-31, 34-38	1	5	9.66	4	8.64
6a		γb	13.18	1-8	5	4	12.04	-	-
6b		γb	13.18	4, 21, 28-31, 33, 38	5	-	-	3	12.19

TABLE 1. (continued)

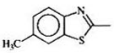
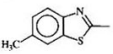
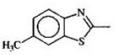
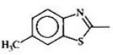
0	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
7a		γ	10.92	1-8	5	4	12.04	-	-
7b		γ	10.92	4, 21, 28-31, 33, 38	5	-	-	3	12.19
8a		C	10.50	1-18	0	4	12.04	3	12.19
8b		C	10.50	4, 9-13, 20, 21, 28-31, 34-38	0	4	12.04	3	12.19
9a		R	9.62	1, 9-14, 19-27	0	-	-	3	12.19
9b		R	9.62	1, 9-14, 20, 21, 32, 39-44	0	4	12.04	-	-
10a		R	8.79	1, 9-12, 14, 19-27	1	-	-	-	-
10b		R	8.79	1, 9-12, 14, 20, 21, 32, 39-44	1	5	9.66	4	8.65
11a		H	9.49	1-18	5	7	4.91	5	5.10
11b		H	9.49	4, 20, 21, 29-31, 34-38	5	7	4.91	5	5.10
12a		γ	8.58	1-8	5	4	12.04	-	-
12b		γ	8.58	4, 21, 28-31, 33, 38	5	-	-	3	12.19
13a		C	7.70	1-18	1	5	9.66	4	8.64
13b		C	7.70	4, 9-12, 20, 21, 28-31, 34-38	1	5	9.66	4	8.64

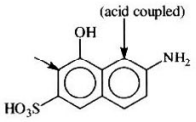
TABLE 1. (continued)

0	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
14a		H	7.24	1-18	5	7	4.91	5	5.10
14b		H	7.24	4, 20, 21, 28-31, 34-38	5	7	4.91	5	5.10
15a		H	6.61	1-18	5	7	4.91	5	5.10
15b		H	6.61	4, 20, 21, 28-31, 34-38	5	7	4.91	5	5.10
16a		R	5.23	1, 14, 19-27	5	-	-	-	-
16b		R	5.23	1, 14, 20, 21, 32, 39-44	5	7	4.91	5	5.10
17a		R	4.60	1, 14, 19-27	5	-	-	-	-
17b		R	4.60	1, 14, 20, 21, 32, 39-44	5	7	4.91	5	5.10
18a		R	4.48	1, 14, 19-27	5	-	-	-	-
18b		R	4.48	1, 14, 20, 21, 32, 39-44	5	7	4.91	5	5.10
19a		C	3.59	4, 20, 21, 28-38	5	7	4.91	5	5.10
19b		C	3.59	1-8, 14-18	5	7	4.91	5	5.10
20a		C	2.97	1-18	5	7	4.91	5	5.10

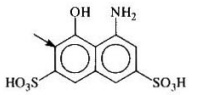
TABLE 1. (continued)

0	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
20b		C	2.97	4, 20, 21, 28-38	5	7	4.91	5	5.10
21a		C	1.92	1-18	5	7	4.91	5	5.10
21b		C	1.92	4, 20, 21, 28-31, 34-38	5	7	4.91	5	5.10

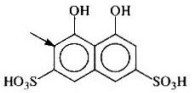
* MTD_0, MTD_1 and MTD_2 - MTD values for starting and final non-connected, and connected maps, respectively, $\hat{A}_1$, $\hat{A}_2$ – calculated dye affinity values for cellulose in both above cases; Y – coupling components: γ, γa, γb - γ acid, γ acid coupled in acidic (respectively basic) medium, H - H acid, C - chromotropic acid, R – R acid



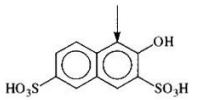
γ acid (γ)



chromotropic acid (C)



R acid (R)



H acid (H)

The presence of sulfonic groups in the coupling component, such as the R acid can generate steric misfit between the dye molecule and the textile fibre and decrease the affinity for cellulose. Detrimental can also be considered the presence of one sulfonic group in ortho position at the naphthalene moiety relative to the azo group, as in case of H or chromotropic acid. Sulfonic groups in some positions attached to the dye molecules produce steric repulsions with the fibre, in accordance to previous studies [9].

TABLE 2. Crossvalidated MTD results*

No.	Cross-validation			
	MTD_n	$\hat{A}_n$	MTD_c	$\hat{A}_c$
1a	2	16.69	-	
1b	-	-	1	17.05
2a	2	17.05	-	-
2b	-	-	2	16.93
3a	-	-	-	-
3b	3	14.43	4	14.91
4a	5	11.87	5	12.84
4b	5	11.87	5	12.84
5a	5	9.47	7	9.47
5b	-	-	7	9.47
6a	5	11.84	-	-
6b	-	-	6	10.93
7a	8	12.12	-	-
7b	-	-	6	12.12
8a	7	13.99	4	13.99
8b	-	-	-	-
9a	-	-	5	13.72
9b	9	11.29	-	-
10a	-	-	-	-
10b	9	9.71	7	9.71
11a	11	4.42	-	-
11b	-	-	8	4.42
12a	9	11.95	-	-
12b	-	-	5	12.63
13a	9	9.85	-	-
13b	-	-	6	9.71
14a	12	4.66	-	-
14b	12	4.66	8	4.66
15a	11	4.66	8	4.73
15b	-	-	8	4.73
16a	-	-	-	-
16b	12	4.73	8	2.93
17a	-	-	-	-
17b	11	4.87	8	3.03
18a	-	-	-	-
18b	12	4.94	8	4.95
19a	13	5.67	9	5.67
19b	13	5.67	9	5.67
20a	10	5.73	-	-
20b	-	-	10	5.73
21a	9	5.83	9	5.83
21b	-	-	9	5.83

*$\hat{A}_n$, $\hat{A}_c$, MTD_n, MTD_c – calculated values of dye affinity and MTD values, in case of non-connected and connected maps, respectively, by 'leave-one-out' crossvalidation procedure

Statistical results indicate the obtained MTD models as stable from statistical point of view and structural dye features favorable for the dye binding to cellulose can be derived.

CONCLUSIONS

MTD calculations are performed for modeling of the dye-textile fibre interactions, for a series of heterocyclic monoazo dyes. For each dye molecule two planar conformations were considered. Good correlation with the dye affinity and predictable models were obtained. Dye binding to cellulose fibre was observed in regions along the axis of the dye molecule. Addition of condensed aromatic nucleus in the heterocyclic dye moiety is favorable for dye adsorption on cellulose. Sulfonic groups in some positions attached to the dye molecules produce steric repulsions with the cellulose fibre.

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