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THIN-LAYER CHROMATOGRAPHIC BEHAVIOUR OF SOME STYRYL CYANINE DYES DERIVED FROM PYRIDINE

LALIT N. PATNAIK*[,a], B. N. PATTANAIK, M. MOHANTY and A. SATAPATHY
Department of Chemistry, Ravenshaw College, Cuttack 753 003, Orissa (India)

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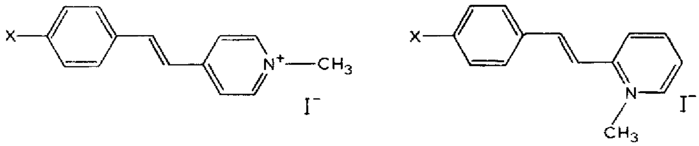
SUMMARY

The chromatographic R_M values for some styryl cyanine iodides derived from pyridine were obtained by thin-layer chromatography using propanol–water–acetic acid solvent systems in various proportions. Linear free energy relationship studies were carried out with some electronic, steric and lipophilic parameters, either singly or in combination with each other. The results indicate that the steric factor has the greatest influence on the chromatographic behaviour. An attempt was made to establish the nature of dye–substrate adsorption by correlation with the theoretical charge densities (CNDO/2 and INDO).

INTRODUCTION

In the past few years, several reports have appeared on the potential usefulness of organic dyes in a number of devices such as photovoltaics, dye lasers and photo- and thermochromic materials. As most of these applications require dyes of exceptionally pure quality, the analytical chemistry of dyes, particularly rapid methods for determining their purity and identity has become of considerable importance. Chromatographic methods (particularly paper and thin-layer chromatography) continue to be popular in this respect. In addition chromatographic methods can also be valuable aids in constitutional analysis and for particular applications chromatographic data can be correlated with activity (*e.g.*, photovoltaic properties). In this context, we have studied the thin-layer chromatographic (TLC) behaviour of some styryl cyanine dyes, which are under investigation for their photovoltaic properties. The dye types studied are shown in Scheme 1.



Scheme 1. Structures of 4-linked pyridine styryl dyes (left) and 2-linked pyridine styryl dyes (right). X = $N(CH_3)_2$; OCH_3; OH; CH_3; H; Cl; and NO_2.

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[a] Present address: State Prevention and Control of Pollution Board, 118/A, Nilakantha Nagar, Unit-VIII, Bhubaneswar 751012, Orissa, India.

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TABLE I

R_F AND R_M VALUES

Dyes	*Mole fraction of water*	*Substituent*													
		$N(CH_3)_2$		OCH_3		OH		CH_3		H		Cl		NO_2	
		R_F	R_M	R_F	R_M	R_F	R_M	R_F	R_M	R_F	R_M	R_F	R_M	R_F	R_M
4-Linked pyridine Styryl	0.445	0.09	1.028	0.06	1.190	0.08	1.091	0.07	1.138	0.07	1.138	0.06	1.190	0.04	1.388
	0.548	0.16	0.718	0.13	0.830	0.14	0.804	0.12	0.859	0.11	0.921	0.11	0.921	0.07	1.114
	0.618	0.24	0.502	0.18	0.652	0.20	0.583	0.19	0.642	0.16	0.706	0.18	0.663	0.10	0.954
	0.669	0.27	0.437	0.22	0.555	0.26	0.461	0.26	0.461	0.23	0.528	0.23	0.537	0.14	0.778
	0.708	0.39	0.202	0.26	0.461	0.32	0.324	0.30	0.361	0.28	0.413	0.30	0.368	0.17	0.684
2-Linked pyridine Styryl	0.445	0.08	1.067	0.06	1.218	0.06	1.163	0.05	1.279	0.04	1.313	0.06	1.190	0.03	1.479
	0.548	0.16	0.730	0.11	0.905	0.13	0.848	0.13	0.831	0.11	0.889	0.12	0.875	0.06	1.163
	0.618	0.24	0.495	0.19	0.632	0.22	0.555	0.22	0.537	0.22	0.555	0.21	0.564	0.10	0.954
	0.669	0.26	0.445	0.19	0.642	0.22	0.546	0.20	0.602	0.19	0.622	0.22	0.555	0.11	0.889
	0.708	0.21	0.564	0.17	0.684	0.19	0.622	0.18	0.673	0.16	0.718	0.19	0.622	0.09	0.99

Attempts were also made to study the structure–adsorption behaviour in the framework of linear free energy relationships (LFER). Reports on this aspect of dyes appear to be very scanty.

EXPERIMENTAL

R_F values of styryl dyes derived from 2- and 4-linked pyridine were determined by TLC using silica gel G (TLC grade, Merck) as sorbent. The TLC plates (20 × 10 cm) were prepared by coating them with a silica gel slurry (20 g of silica gel in 50 ml of water) to a thickness of 0.25 mm. The TLC plates were dried at room temperature and then activated at 110°C for 15 min.

The chromatographic chambers were saturated with the appropriate composition of water–*n*-propanol–acetic acid (saturation time, 24 h; temperature of the chamber, 30°C). Initial experiments with water–*n*-propanol mixtures resulted in the formation of streaks, which could be avoided by the addition of acetic acid at a concentration below 2%. The presence of acetic acid was taken into account in calculating the mole fraction of water, at different values of which the R_F values are reported below.

The activated plates were spotted with the dye solution in acetone and then conditioned in the solvent-saturated chromatographic chamber for 10–15 min before development started. All the experiments were carried out in duplicate. The spots were detected in an iodine chamber and the R_F values were measured.

RESULTS AND DISCUSSION

Chromatographic parameters

The theoretical basis for the relationship between R_F values and chemical structure was first proposed by Consden *et al.*[1]. Subsequently, Martin[2] deduced that for ideal solutions the partition coefficient, P, of a substance A between two phases is related to the free energy required to transport 1 mole of A from one phase to another.

Bate-Smith and Westall[3] introduced the term R_M, defined as

$$R_M = \log\left(\frac{1}{R_F} - 1\right) \tag{1}$$

Boyce and Milborrow[4] investigated the theoretical basis for the relationship between the partition coefficient and R_M values and pointed out that the R_M value for a substituent is a free energy-related term analogous to π used by Hansch and Fujita[5], and consequently it is possible to correlate R_M with other free energy-related terms. There have been various reports of a very good correlation between R_M and π values[6]. It was pointed out, however, that R_M cannot be considered as an expression of the true partition coefficient as it does not take into account the ratio of the cross-sectional areas of the mobile and stationary phases[7]. We therefore carried out some of the correlations using log R_F. It was found, however, that there is hardly any significant difference between the results obtained with log R_F and R_M. The following discussions therefore pertain to the results obtained with R_M.

Solvent effects

R_F values were determined at five different compositions of water–*n*-propanol–acetic acid. The R_F values were found to increase with increasing water content, *i.e.*, with increasing solvent polarity (Table I) and the correlation of R_M with the mole fraction of water (x) was excellent for 4-linked pyridine-substituted styryl dyes. With the 2-linked pyridine dyes the R_F values increased with increasing water content up to a certain point and then decreased. For different substituted compounds this point was reached at different mole fractions of water. However, a value of 0.708 seems to be the limit beyond which the R_F values decrease in all instances. This observation indicates that perhaps there is a change in the retention mechanism. Similar observations have been reported in connection with the reversed-phase chromatographic behaviour of steroids[8,9]. The correlation of R_M of the 2-linked pyridine dyes with x up to a value of 0.708 was found to be satisfactory (Table II).

Linear free energy relationships

The reported correlations between chromatographic behaviour and π may be interpretated as the transport process being the step that determines the chromatographic activity[10]. Such correlations, however, do not preclude the possibility that the electronic properties and the steric arrangement of the molecule could also be important factors for interaction with the stationary phase in partition chromatography. In other words, it should be established which of the lipophilicity, electronic factors and stereochemistry of the molecules is the most important factor with regard to the chromatographic activity, either individually or combined. Accordingly, we studied four types of correlations:

(i) correlations with Hammet or related substituent parameters that are supposed to reflect the polar and/or resonance effects of the substituents[11];

(ii) correlations with the lipophilic parameter[5];

(iii) correlations with Taft's[12] E_s and Charton's[13–15] v steric parameters;

(iv) correlations with combinations of (i) or (ii) with the steric parameters in (iii).

Correlations were carried out with the following equations:

for single-parameter correlations:

$$R_M \text{ (or } \log R_F) = as + b \tag{2}$$

TABLE II

CORRELATION RESULTS WITH $R_M = ax + b$

x = Mole fraction of water.

Substituent	*4-Linked pyridine styryl dyes*				*2-Linked pyridine styryl dyes*			
	S	*R*	*a*	*b*	*S*	*R*	*a*	*b*
$N(CH_3)_2$	0.051	0.993	−2.963	2.248	0.124	0.938	−2.184	1.965
OCH_3	0.039	0.995	−2.738	2.374	0.111	0.950	−2.22	2.143
OH	0.013	0.999	−2.894	2.382	0.120	0.946	−2.312	2.128
CH_3	0.017	0.999	−3.002	2.486	0.168	0.916	−2.487	2.271
H	0.035	0.996	−2.797	2.413	0.175	0.913	−2.52	2.325
Cl	0.030	0.998	−3.101	2.589	0.119	0.951	−2.419	2.207
NO_2	0.017	0.999	−2.682	2.587	0.107	0.948	−2.099	2.350

for two-parameter correlations:

$$R_M \text{ (or } \log R_F) = as_1 + bs_2 + c \quad (3)$$

where s, s_1 and s_2 are appropriate substituent parameters.

Single parameter correlations

Very poor correlations were obtained with both dye series with Hansch and Fujita's lipophilic parameter π (Table III).

As has already been pointed out, the parameter R_M, which is assumed to be a measure of lipophilic character, has been shown to correlate well with π for a large number of systems. The lack of any correlation in this study may be due to one or more of the following reasons. The transport process perhaps is not the most crucial factor in the chromatographic behaviour. The chromatographic process evidently is not analogous to the octanol water system and the low correlation between π and R_M may be due to the electronic effects of the substituent. As the dyes are ionic in nature, they are likely to undergo dissociation in the aqueous–organic chromatographic system. It has been pointed out earlier that an R_M–π correlation is valid only if the degree of dissociation is taken into account. One way to meet the problem of the effect of dissociation is to include the Hammet σ constant in the correlation equation[16].

Correlations with polar substituent parameters

Correlations were attempted with four types of electronic parameters:

(i) the original Hammet σ constants derived from substituted benzoic acids;

(ii) σ_p^+, derived from the solvolysis of dimethyl diphenyl carbinyl chlorides in 90% aqueous acetone at 25°C[17];

(iii) σ_p^-, obtained from the reaction of phenols and anilines[18];

(iv) σ^0, derived by averaging values from selected reactions involving substrates in which a methylene group has been interposed between the reaction centre and the substituent to prevent an overestimation of direct conjugation effects[19–21].

The results in Tables IV and V indicate that the correlations are poor, or at the most fair in a few instances. Particular attention may be drawn to the results with σ_p^+. The poor quality of the correlation with this parameter would lead one to believe that the adsorption process perhaps does not involve an electron-deficient centre and hence not an electron-rich bonding site on the silica gel. If this were true, a substantial

TABLE III

CORRELATION RESULTS WITH $R_M = a\pi + b$

Mole fraction of water (x)	*4-Linked pyridine styryl dyes*				*2-Linked pyridine styryl dyes*			
	S	*R*	*a*	*b*	*S*	*R*	*a*	*b*
0.445	0.114	0.5391	−0.036	1.180	0.128	0.5123	−0.022	1.268
0.548	0.124	0.5075	−0.016	0.904	0.124	0.6241	−0.078	0.897
0.618	0.142	0.5386	−0.045	0.688	0.158	0.4727	−0.113	0.660
0.669	0.123	0.5846	−0.060	0.538	0.132	0.5873	−0.066	0.625
0.708	0.136	0.5900	−0.070	0.417	0.145	0.5845	−0.071	0.699

TABLE IV

CORRELATION RESULTS WITH $R_M = as + b$ FOR 4-LINKED PYRIDINE STYRYL DYES

s	*Mole fraction of water (x)*	S	R	a	b	$\hat{R}^2$
σ	0.445	0.049	0.931	0.224	1.181	0.88225
	0.548	0.023	0.987	0.259	0.900	
	0.618	0.055	0.945	0.286	0.691	
	0.669	0.059	0.921	0.247	0.545	
	0.708	0.085	0.866	0.252	0.427	
σ^+	0.445	0.0.70	0.854	0.133	1.213	0.76670
	0.548	0.036	0.969	0.169	0.940	
	0.618	0.071	0.907	0.181	0.734	
	0.669	0.082	0.842	0.145	0.580	
	0.708	0.102	0.796	0.149	0.463	
σ^0	0.445	0.047	0.938	0.251	1.160	0.86707
	0.548	0.034	0.972	0.281	0.877	
	0.618	0.058	0.938	0.315	0.664	
	0.669	0.054	0.933	0.280	0.522	
	0.708	0.083	0.872	0.283	0.403	
σ^-	0.445	0.058	0.903	0.116	1.202	0.84515
	0.548	0.019	0.992	0.141	0.924	
	0.618	0.053	0.950	0.157	0.717	
	0.669	0.068	0.893	0.129	0.568	
	0.708	0.088	0.854	0.134	0.450	

TABLE V

CORRELATION RESULTS WITH $R_M = as + b$ FOR 2-LINKED PYRIDINE STYRYL DYES

s	*Mole fraction of water (x)*	S	R	a	b	$\hat{R}^2$
σ	0.445	0.076	0.859	0.220	1.266	0.78003
	0.548	0.068	0.904	0.253	0.909	
	0.618	0.102	0.872	0.314	0.622	
	0.669	0.080	0.905	0.302	0.603	
	0.708	0.086	0.875	0.271	0.709	
σ^+	0.445	0.074	0.868	0.150	1.300	0.67299
	0.548	0.090	0.823	0.148	0.945	
	0.618	0.130	0.778	0.176	0.665	
	0.669	0.098	0.800	0.144	0.669	
	0.708	0.099	0.830	0.168	0.749	
σ^0	0.445	0.082	0.833	0.233	1.247	0.77860
	0.548	0.060	0.926	0.291	0.885	
	0.618	0.088	0.905	0.368	0.591	
	0.669	0.082	0.865	0.270	0.612	
	0.708	0.085	0.880	0.303	0.684	
σ^-	0.445	0.064	0.904	0.129	1.288	0.76836
	0.548	0.074	0.884	0.133	0.933	
	0.618	0.111	0.846	0.163	0.651	
	0.669	0.083	0.861	0.131	0.657	
	0.708	0.082	0.887	0.150	0.735	

improvement in the correlation should have been observed with σ_p^-. However, although there is an improvement with respect to σ_p^+, the correlations are still far from satisfactory. We therefore conclude that the polar factors alone cannot adequately account for the substituent effect on the chromatographic behaviour of the dyes.

Tables VI and VII give the results of the correlations with σ and π. Considering that the same number of data points are used for the two-parameter correlations, the apparent improvement in the correlations (increased average $\hat{R}^2$ values) is only marginal and not much significance need be attached to this, as is evident from the F values (the significance of the correlations being less than 95% in almost all instances).

Correlation with steric parameters

In an attempt to find a possible connection between lipophilicity and steric substituent constants, Tichy[10] reported that the steric constants E_s and v have the greatest chance of being independent of lipophilic substituent constants. As no correlation was found between the present set of chromatographic data and the lipophilic substituent constant π, we attempted a correlation of R_M (or log R_F) with E_s and v in preference to other steric and sterimole parameters.

Charton's[13–15] steric substituent constant, v, is based on the van der Waals radii and is defined by

$$v_X = r_X - r_H = r_X - 1.20 \qquad (4)$$

TABLE VI

CORRELATION RESULTS WITH $R_M = a\pi + bs_2 + c$ FOR 4-LINKED PYRIDINE STYRYL DYES

s_2	*Mole fraction of water*	S	R	a	b	c	F	$\hat{R}^2$
σ	0.445	0.046	0.941	−0.011	0.182	1.172	5.155	0.9030
	0.548	0.061	0.938	−0.006	0.259	0.898	4.882	
	0.618	0.055	0.964	−0.028	0.285	0.685	8.296	
	0.669	0.052	0.960	−0.032	0.245	0.537	7.837	
	0.708	0.066	0.948	−0.037	0.250	0.417	5.915	
σ^+	0.445	0.066	0.872	−0.040	0.155	1.192	2.116	0.9074
	0.548	0.016	0.996	−0.044	0.177	0.930	82.834	
	0.618	0.050	0.970	−0.074	0.195	0.717	10.614	
	0.669	0.059	0.948	−0.085	0.160	0.561	5.915	
	0.708	0.085	0.972	−0.095	0.165	0.441	11.407	
σ^0	0.445	0.053	0.946	−0.009	0.248	1.158	5.677	0.8936
	0.548	0.037	0.978	0.015	0.287	0.880	14.653	
	0.618	0.067	0.946	−0.011	0.311	0.662	5.677	
	0.669	0.057	0.952	−0.031	0.269	0.515	6.449	
	0.708	0.089	0.903	−0.040	0.269	0.394	2.945	
σ^-	0.445	0.057	0.939	−0.040	0.118	1.191	4.970	0.922
	0.548	0.010	0.998	−0.022	0.142	0.918	166.167	
	0.618	0.042	0.979	−0.051	0.158	0.704	15.375	
	0.669	0.054	0.957	−0.065	0.131	0.551	7.256	
	0.708	0.078	0.927	−0.075	0.136	0.431	4.073	

TABLE VII

CORRELATION RESULTS WITH $R_M = a\pi + bs_2 + c$ FOR 2-LINKED PYRIDINE STYRYL DYES

s_2	*Mole fraction of water (x)*	*S*	*R*	*a*	*b*	*c*	*F*	$\hat{R}^2$
σ	0.445	0.086	0.880	−0.010	0.219	1.264	2.228	0.8231
	0.548	0.103	0.849	−0.042	0.251	0.899	1.721	
	0.618	0.083	0.946	−0.061	0.310	0.606	5.677	
	0.669	0.084	0.907	−0.035	0.238	0.625	3.092	
	0.708	0.068	0.950	−0.038	0.269	0.699	6.171	
σ^+	0.445	0.065	0.934	−0.038	0.111	1.285	4.556	0.8834
	0.548	0.053	0.962	−0.104	0.166	0.922	8.275	
	0.618	0.086	0.941	−0.143	0.201	0.633	5.155	
	0.669	0.077	0.924	−0.091	0.161	0.649	3.893	
	0.708	0.075	0.938	−0.10	0.185	0.726	4.882	
σ^0	0.445	0.095	0.853	0.004	0.231	1.248	2.088	0.8612
	0.548	0.052	0.964	−0.048	0.275	0.874	8.762	
	0.618	0.079	0.951	−0.075	0.342	0.574	6.307	
	0.669	0.049	0.964	−0.031	0.269	0.515	8.762	
	0.708	0.089	0.903	−0.040	0.269	0.394	2.945	
σ^-	0.445	0.070	0.924	−0.027	0.129	1.281	3.898	0.8983
	0.548	0.045	0.973	−0.084	0.136	0.911	11.681	
	0.618	0.074	0.957	−0.119	0.166	0.620	7.189	
	0.669	0.073	0.932	−0.071	0.134	0.639	4.377	
	0.708	0.067	0.952	−0.077	0.153	0.715	6.441	

where r_X and r_H are the van der Waal radii of X and H groups, respectively. For tetrahedral substituents such as methyl and *tert.*-butyl, the calculated values of the minimum van der Waal's radii were used. The results of the correlations of v and E_s with R_M for both series of dyes are given in Table VIII.

All correlations with E_s (Table VIII) were very poor. The E_s values are derived from kinetic data and there can be two possibilities for the failure: first, the E_s parameters may not have been correctly defined and may contain not only steric but also electrical effects[13–15]; second, they may be inapplicable in the pesent context as they do not correctly represent the "shape" in the particular environment under study.

On the other hand, although Charton's v parameter has been reported basically with the same properties and limitations, we found that in the present instance correlations of R_M with v are fairly satisfactory and much superior to those obtained with E_s (Table VIII). As the values are derived from van der Waals radii, it is reasonable to suppose that they represent a purer form of the steric parameters.

The results of the combination of a polar (σ) or a lipophilic (π) parameter with v are presented in Tables IX and X.

With the same number of data points, as expected there is an increase in the correlation coefficients. The improvement in the correlations, however, can be concluded from the F values, most of which represent the 95% significance level. Inclusion of a polar or lipophilic parameter leads to similar correlation results. This further corroborates our contention that the steric factor is predominant in the chromatographic behaviour.

The adsorption properties of silica gel are known to be determined by the

TABLE VIII

CORRELATION RESULTS WITH $R_M = a\nu + b$ AND $R_M = aE_s + b$

Dyes	*Mole fraction of water (x)*	$a\nu + b = R_M$				$aE_s + b = R_M$			
		S	*R*	*a*	*b*	*S*	*R*	*a*	*b*
4-Linked pyrydine styryl	0.445	0.032	0.972	−0.027	1.167	0.044	0.671	0.060	1.065
	0.548	0.041	0.959	−0.029	0.886	0.061	0.581	0.012	0.851
	0.618	0.022	0.992	−0.035	0.672	0.049	0.625	−0.045	0.712
	0.669	0.035	0.973	−0.031	0.529	0.051	0.578	−0.006	0.517
	0.708	0.038	0.974	−0.034	0.408	0.057	0.646	−0.064	0.476
2-Linked pyridine styryl	0.445	0.048	0.946	−0.029	1.251	0.060	0.729	−0.116	1.396
	0.548	0.027	0.986	−0.033	0.892	0.035	0.634	−0.034	0.916
	0.618	0.044	0.978	−0.043	0.599	0.042	0.579	−0.008	0.579
	0.669	0.029	0.984	−0.034	0.616	0.041	0.721	−0.075	0.700
	0.708	0.028	0.931	−0.036	0.688	0.032	0.838	−0.107	0.814

TABLE IX

CORRELATION RESULTS WITH $R_M = a\nu + bs_2 + c$ FOR 4-LINKED PYRIDINE STYRYL DYES

s_2	*Mole fraction of water (x)*	*S*	*R*	*a*	*b*	*c*	*F*	$\hat{R}^2$
σ	0.445	0.034	0.967	−0.016	0.058	1.166	9.604	0.9648
	0.548	0.018	0.995	−0.009	0.185	0.895	66.167	
	0.618	0.021	0.995	−0.029	0.057	0.675	66.167	
	0.669	0.039	0.978	−0.027	0.035	0.531	14.653	
	0.708	0.045	0.976	−0.044	−0.09	0.404	13.391	
σ^+	0.445	0.038	0.960	−0.021	0.009	1.166	7.837	0.9661
	0.548	0.013	0.997	−0.015	0.099	0.915	110.611	
	0.618	0.017	0.996	−0.030	0.039	0.684	82.834	
	0.669	0.040	0.977	−0.032	−0.008	0.527	13.995	
	0.708	0.037	0.984	−0.042	−0.052	0.393	20.335	
σ^0	0.445	0.036	0.963	−0.016	0.059	1.161	8.887	0.9609
	0.548	0.031	0.984	−0.012	0.176	0.879	20.335	
	0.618	0.024	0.993	−0.032	0.030	0.671	47.120	
	0.669	0.038	0.978	−0.026	0.054	0.527	14.653	
	0.708	0.038	0.983	−0.045	−0.116	0.413	19.109	
σ^-	0.445	0.037	0.975	−0.027	0.002	1.168	12.835	0.9727
	0.548	0.011	0.998	−0.009	0.103	0.913	166.167	
	0.618	0.019	0.996	−0.028	0.038	0.682	82.834	
	0.669	0.040	0.977	−0.033	−0.010	0.527	13.995	
	0.708	0.035	0.985	−0.045	−0.060	0.392	21.723	
π	0.445	0.036	0.963	−0.023	0.014	1.167	8.887	0.9570
	0.548	0.038	0.976	−0.031	0.033	0.893	13.391	
	0.618	0.022	0.994	−0.036	0.013	0.675	55.056	
	0.669	0.038	0.978	−0.030	−0.012	0.526	14.653	
	0.708	0.041	0.980	−0.034	−0.015	0.405	16.168	

TABLE X

CORRELATION RESULTS WITH $R_M = av + bs_2 + c$ FOR 2-LINKED PYRIDINE STYRYL DYES

s_2	*Mole fraction of water (x)*	*S*	*R*	*a*	*b*	*c*	*F*	$\hat{R}^2$
σ	0.445	0.053	0.957	−0.034	−0.043	1.249	7.256	0.9692
	0.548	0.027	0.990	−0.035	−0.021	0.891	32.834	
	0.618	0.045	0.984	−0.053	−0.102	0.594	20.335	
	0.669	0.018	0.996	−0.047	−0.125	0.610	82.834	
	0.708	0.022	0.995	−0.048	−0.100	0.684	66.167	
σ^+	0.445	0.084	0.886	−0.045	−0.110	1.219	0.113	0.9431
	0.548	0.031	0.987	−0.037	−0.032	0.883	25.142	
	0.618	0.030	0.993	−0.055	−0.089	0.573	47.120	
	0.669	0.023	0.994	−0.041	−0.053	0.600	55.056	
	0.708	0.029	0.991	−0.042	−0.031	0.680	36.538	
σ^0	0.445	0.048	0.965	−0.042	−0.139	1.256	9.027	0.9524
	0.548	0.031	0.987	−0.032	0.013	0.892	25.142	
	0.618	0.092	0.931	−0.046	−0.036	0.601	4.337	
	0.669	0.011	0.999	−0.049	−0.157	0.622	332.833	
	0.708	0.019	0.996	−0.050	−0.131	0.694	82.834	
σ^-	0.445	0.054	0.955	−0.024	0.027	1.258	6.911	0.9697
	0.548	0.028	0.990	−0.039	−0.033	0.883	32.834	
	0.618	0.031	0.992	−0.060	−0.090	0.576	41.167	
	0.669	0.020	0.995	−0.045	−0.060	0.601	66.167	
	0.708	0.029	0.991	−0.044	−0.035	0.679	36.538	
π	0.445	0.051	0.960	−0.031	0.028	1.258	7.837	0.9684
	0.548	0.027	0.990	−0.031	−0.027	0.886	32.834	
	0.618	0.03	0.993	−0.040	−0.048	0.589	47.120	
	0.669	0.032	0.987	−0.033	−0.013	0.613	25.142	
	0.706	0.030	0.990	−0.036	−0.013	0.686	32.834	

number of hydroxyl groups on the surface[22], which in turn implies that the binding site on the silicagel surface is possibly the hydroxyl group through hydrogen bonding. Now we need to address the question of what the state of the substrate molecules is, *i.e.*, whether on the silica gel substrate adsorptions take place in a point-to-point manner or whether it is some kind of surface-to-surface stacking. Although more elaborate experiments must be designed in order to answer this question unequivocally, we would like to draw a broad, qualitative conclusion from our theoretical (quantum mechanical PCILO) studies on the conformation of these dyes. It has been observed with 4-linked pyridine dyes that the deviation of the end groups (benzene and pyridine) from coplanarity decreaes in the order $N(CH_3)_2 > OH > H > CH_3 > NO_2$. With 2-linked pyridine dyes the deviation from coplanarity is much more pronounced in terms of both the twist angle and the energy barrier with respect to the planar conformation. The deviation from coplanarity decreases approximately in the order $OH > H > CH_3 \approx N(CH_3)_2 > NO_2$. We find that the R_F values vary approximately in the reverse order, that is, the less planar a molecule is, the more strongly it is adsorbed by silica gel (lower R_F value) and *vice-versa*. From this we may perhaps preclude the possibility of surface-to-surface stacking, and hence a relatively smaller influence of the degree of planarity on the chromatographic behaviour of the dyes.

TABLE XI

CORRELATION RESULTS WITH $R_M = a(\text{CNDO/2}) + bv + c$ AND $R_M = a(\text{INDO}) + bv + c$

Substituents included in these correlations are $N(CH_3)_2$, OH, CH_3, H and NO_2. The value for $N(CH_3)_2$ was obtained by extrapolation from the best correlations in Table VIII.

Dyes	*Mole fraction of water (x)*	$a(CNDO/2) + bv + c = R_M$					$a(INDO) + bv + c = R_M$				
		S	*R*	*a*	*b*	*c*	*S*	*R*	*a*	*b*	*c*
4-Linked pyridine styryl	0.445	0.014	0.9987	0.052	−0.027	1.144	0.014	0.9987	0.034	−0.028	1.146
	0.548	0.023	0.9971	−0.197	−0.033	0.911	0.023	0.9970	−0.148	−0.033	0.905
	0.618	0.023	0.9977	−0.139	−0.037	0.695	0.023	0.9977	−0.106	−0.037	0.691
	0.669	0.046	0.9864	0.187	−0.026	0.498	0.047	0.9861	0.136	−0.026	0.605
	0.708	0.019	0.9985	−0.035	−0.037	0.397	0.019	0.9985	−0.035	−0.037	0.396
2-Linked pyridine styryl	0.445	0.019	0.9981	−0.500	−0.037	1.342	0.024	0.9972	−0.350	−0.036	1.317
	0.548	0.022	0.9977	0.207	−0.030	0.852	0.022	0.9978	0.159	−0.031	0.858
	0.618	0.046	0.9924	0.549	−0.030	0.521	0.048	0.9918	0.402	−0.031	0.540
	0.669	0.003	0.9996	−0.053	−0.035	0.624	0.004	0.99994	−0.037	−0.035	0.622
	0.708	0.025	0.9971	−0.024	−0.034	0.712	0.025	0.9971	−0.020	−0.034	0.712

From the correlation results with σ_p^+ and σ_p^-, we had earlier concluded that perhaps an electron-rich centre is involved in the chromatographic binding with silica gel (evidently an $-O-H\cdots X$ type of hydrogen bonding). To test this hypothesis, correlations were carried out with ν in combination with the electron densities (obtained by CNDO/2 and INDO methods). The excellent results obtained (Table XI) bear out this possibility.

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