

Notes

Applicability of Williams-Norrington model for quantitative structure spectra relationship

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Received 28 December 1994, revised and accepted
6 March 1995

Williams-Norrington equation has been utilised to correlate the absorption spectra with the substituent parameters in 5-arylidene 1,3-diphenyl 2-thiobarbituric acids. The regression model with three substituent parameters reveals a significant participation of steric parameter in the quantitative structure spectra relationship.

The model suggested by Swain and Lupton¹ and modified by Williams and Norrington² (Eq. 1) has been applied successfully to predict dissociation constants^{3,4}

$$P = \alpha_i f_j F_k + \beta_i r_j R_k + P_{ijk}^0 \quad \dots (1)$$

and reactivities^{5,6} of various substituted aromatics. In Eq. (1), P is the dependent parameter; F_k and R_k are the position independent field and resonance parameters of the substituent, k , f_j and r_j are the positional weightage factors ($f_{ortho} = 1.248$, $f_{meta} = 0.980$, $f_{para} = r_{para} = 1$, $r_{ortho} = 0.863$ and $r_{meta} = 0.347$)² for the substituents at the respective position; α_i and β_i are the sensitivities of the field and resonance contribution in a particular system, i , respectively. Though these parameters have been generated from reaction systems, they fit in well for predicting NMR data⁷. In this note we have made an attempt to examine the applicability of model-1 in quantitative structure spectra relationship (QSSR) for some α,β -unsaturated carbonyl compounds.

In continuation of our studies on the synthesis of heterocycles based on the reaction of thiobarbituric acids with suitable substrates^{8,9,10} we have synthesised some 5-arylidino-2-thiobarbituric acids which contain unsaturated carbonyl system. These molecules are subjected to QSSR study by modifying model-1.

Experimental

The 5-arylidino 1,3-diphenyl thiobarbituric acids were synthesized from 1,3-diphenyl thiobarbituric acid and substituted benzaldehydes by earlier

reported method⁸. The analytical data of the compounds are presented in Table 1. Dioxane was purified to spectroscopic grade using the technique of Eigenberger.

Melting points are uncorrected. Absorption spectra were recorded in dioxane medium on a Hitachi-200 UV-vis spectrophotometer at $303 \pm 0.2^\circ$ and the NMR spectra were recorded on a WH-270 FT-NMR spectrometer in $CDCl_3$.

Results and discussion

The NMR spectra of the arylidene derivatives show two distinct complex peaks at 7.3 to 7.5 δ and 7.5 to 7.7 δ values indicating the compounds to be unsymmetrical with respect to the N-phenyl rings. For *para*-substituted arylidenes, two doublets ($J \approx 7.8$ Hz) at ~ 7.0 δ and 8.5 δ are the characteristic peaks for the arylidene protons. For *ortho* and *meta*-substituted derivatives, complex peaks at ~ 8.0 δ are observed. The olefinic proton peak is found in the low field region at 8.96 δ . The substituents in the benzene ring do not show any significant effect on the chemical shift value of this proton.

The absorption maxima of these compounds (Table 2) can clearly differentiate the electron-withdrawing and electron-donating substituents. The compounds with electron-donating groups have substantially red shifted spectra (from -H to *p*-OMe, the shift is 51 nm) whereas compounds with electron-withdrawing groups have blue shifted spectra. The absorption maxima have been subjected to multiple regression analysis using Eq. (1). The values of regression coefficients have been determined and the corresponding Eq. (2) is obtained.

$$\lambda_{max} = 368.034 - 3.223 f_j F_k - 84.578 r_j R_k \quad \dots (2)$$

$$n = 10 \quad R^2 = 0.9417 \quad s = 6.3715 \quad F = 51.47$$

where n refers to number of data points, R refers to regression constant, s error of estimate and F is the level of confidence test¹².

To examine, if any steric contribution due to *ortho* substituent affects the absorption maxima, a third parameter, steric density (SD)³ has been incorporated by modifying Eq. (1). Except *ortho* substituents for all the substituents $SD_k = 0$. The regression equation, thus

$$P = \alpha_i f_j F_k + \beta_i r_j R_k + \gamma SD_k + P_{ijk}^0 \quad \dots (3)$$

Table 1—Characterization data of 5-arylidino 1,3-diphenyl 2-thiobarbituric acids

Empirical formula	Substituents in arylidino nucleus	M.pt. (°C)	Yield (%)	Found (Calcd.), %		
				C	H	S
C ₂₃ H ₁₆ N ₂ O ₂ S	H	250	64	71.6 (71.9)	4.0 (4.2)	7.9 (8.3)
C ₂₃ H ₁₅ N ₂ O ₂ SCl	<i>p</i> -Cl	218	58	66.1 (66.0)	3.6 (3.6)	7.1 (7.7)
C ₂₄ H ₁₈ N ₂ O ₃ S	<i>p</i> -Me	220	72	72.2 (72.4)	4.6 (4.5)	7.9 (8.0)
C ₂₄ H ₁₈ N ₂ O ₃ S	<i>p</i> -OMe	241	60	69.4 (69.6)	4.2 (4.3)	7.5 (7.7)
C ₂₃ H ₁₅ N ₃ O ₄ S	<i>p</i> -NO ₂	255	60	64.4 (64.3)	3.4 (3.5)	7.0 (7.5)
C ₂₃ H ₁₅ N ₃ O ₄ S	<i>m</i> -NO ₂	180	56	64.1 (64.3)	3.6 (3.5)	7.1 (7.5)
C ₂₃ H ₁₅ N ₃ O ₄ S	<i>o</i> -NO ₂	232	35	64.4 (64.3)	3.3 (3.5)	7.2 (7.5)
C ₂₃ H ₁₅ N ₂ O ₂ SCl	<i>o</i> -Cl	241	42	65.8 (66.0)	3.4 (3.6)	7.2 (7.7)
C ₂₄ H ₁₈ N ₂ O ₃ S	<i>o</i> -OMe	209	50	72.1 (69.6)	4.6 (4.3)	7.8 (7.7)
C ₂₃ H ₁₆ N ₂ O ₃ S	<i>o</i> -OH	202	70	69.1 (69.0)	3.8 (4.0)	7.7 (8.0)

Table 2—Absorption maxima (λ_{\max}), Swain Lupton parameters with Williams-Norrington's weightage factors and Steric Density (*SD*) values of 5-arylidino 1,3-diphenyl 2-thiobarbituric acids

Empirical formula	Substituent in arylidino nucleus	λ_{\max} (nm) Found (Calcd.)	Substituent parameters		
			$f_j F_k$	$r_j R_k$	<i>SD</i>
C ₂₃ H ₁₆ N ₂ O ₂ S	H	368 (367)	0	0	0
C ₂₃ H ₁₅ N ₂ O ₂ SCl	<i>p</i> -Cl	381 (382)	0.69	-0.161	0
C ₂₄ H ₁₈ N ₂ O ₂ S	<i>p</i> -Me	379 (379)	-0.052	-0.141	0
C ₂₄ H ₁₈ N ₂ O ₃ S	<i>p</i> -OMe	419 (413)	0.413	-0.500	0
C ₂₃ H ₁₅ N ₃ O ₄ S	<i>p</i> -NO ₂	356 (354)	1.019	0.155	0
C ₂₃ H ₁₅ N ₃ O ₄ S	<i>m</i> -NO ₂	365 (364)	1.086	0.054	0
C ₂₃ H ₁₅ N ₃ O ₄ S	<i>o</i> -NO ₂	351 (348)	1.384	0.134	2.448
C ₂₃ H ₁₅ N ₂ O ₂ SCl	<i>o</i> -Cl	370 (372)	0.861	-0.139	2.664
C ₂₄ H ₁₈ N ₂ O ₃ S	<i>o</i> -OMe	405 (402)	0.515	-0.431	1.548
C ₂₃ H ₁₆ N ₂ O ₃ S	<i>o</i> -OH	408 (411)	0.608	-0.555	2.270

obtained, can be represented by Eq. (4),

$$\gamma_{\max} = 366.5644 + 1.939 f_j F_k - 91.8254 r_j R_k - 3.4626 SD_k \quad \dots (4)$$

$$n = 10, R^2 = 0.9628, s = 5.494, F = 62.8$$

On analyzing Eqs (2) and (4), the contribution of resonance factor is found to be very high than that of field factor. The percentage composition of field (P_F), resonance (P_R) and steric (P_S) effects have been calculated using Eq. (5),

$$P_F = \alpha_i / (\alpha_i + \beta_i + \gamma_i), P_R = \beta_i / (\alpha_i + \beta_i + \gamma_i), P_S = \gamma_i / (\alpha_i + \beta_i + \gamma_i) \quad \dots (5)$$

and are found to be 94.44, 1.99 and 3.56 respectively. This suggests that the resonance factor of the substituents has a significant contribution in absorption maximum of arylidene compounds. The addition of steric parameter improved the regression coefficient to a significant extent. This is also reflected from a higher percentage composition value of steric effect over resonance effect. The calculated absorption maxima of arylidenes using Eq. (4) are given in Table 2. A good agreement with the observed values is noted indicating that Williams-Norrington model appears to be a

general character for quantitative structure spectra relationship in $\alpha:\beta$ -unsaturated systems.

Acknowledgement

One of us (BKM) thanks the INSA, New Delhi, for the award of a visiting fellowship at I I Sc, Bangalore. We also thank Prof. C L Khetrapal and S Vivekanandan for recording NMR spectra.

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