

SPECTRAL STUDY ON BARBITURIC AND THIOBARBITURIC ACIDS

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ABSTRACT

The shifts in peak locations in the electronic spectra of barbituric and thiobarbituric acids have been correlated with different solvent polarity parameters. An estimate of band position for gas phase spectra has been compared with PPP-method calculated values.

INTRODUCTION

BARBITURATES and thiobarbiturates are widely used in medicine, principally as hypnotic drugs. They contain an amide linkage that can undergo enolization to varying degrees. A study of the electronic spectra of these systems in different organic solvents may provide information about their different interactions which is of fundamental importance in determining the action of these drugs.

Various solvent dependent phenomena have been recently studied¹⁻⁸, and different mechanisms for the interaction between solute and solvent molecules have been proposed⁹⁻¹².

In the present paper the electronic spectra of barbituric acid (BA) and thiobarbituric acid (TBA) in different organic solvents have been analyzed using the multiple linear regression technique relating the shift in peak position to different solvent polarity parameters. Estimates of peak locations in the gas phase spectra have been compared with PPP-method calculated values.

EXPERIMENTAL

The electronic absorption spectra were obtained using a Pye-Unicam SP-1750 spectrophotometer, and the solvents used were of spectroquality. Barbituric and thiobarbituric acids were obtained as reagent grade materials.

METHODS OF CALCULATION

(a) *Data analysis*: In the present study; the observed peak location in a given solvent (Y) has been expressed by the following multiparameter equation:

$$Y = a_0 + a_1 X_1 + a_2 X_2 + \dots + a_n X_n, \quad (1)$$

which is amenable to solution for the intercept a_0 and the coefficients a_i by multiple regression techniques. The intercept a_0 has been assumed⁸ to be an estimate of the peak position for gas phase spectra.

In a three-parameter equation we selected the independent variables X_1 , X_2 and X_3 to be the solvent interaction mechanisms E , M and N ⁴. The empirical solvent polarity parameter E is sensitive to both solvent-solute hydrogen bonding and to dipolar interactions^{4, 13}. The parameter M is a measure of the solute permanent dipole-solvent induced dipole interactions^{4, 13} defined as follows:

$$M = (n^2 - 1)/2n^2 + 1, \quad (2)$$

where n is the solvent refractive index. The parameter N is a measure of the permanent dipole-permanent dipole interactions^{4, 13} given the following expression

$$N = \frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \quad (3)$$

A Fortran IV program¹⁴ which utilizes the gauss-elimination method was used to solve the sets of multilinear equations using the standard matrix methods.

(b) *PPP-method*: The ground state properties and different singlet-singlet electronic transitions for BA and TBA have been calculated using the PPP-method¹⁵⁻¹⁷, with full CI calculations including only all singly excited configurations. The resonance integrals, VSIP's and the one-centre electron repulsion integrals have been assigned their well-known standard values^{18, 19} while the two-centre electron repulsion integrals have been calculated using the Mataga-Nishimoto approximation²⁰. A Fortran IV program²¹ for the PPP-method has been used and the molecules assigned their experimental geometries²². Calculations have been done on a PDP 11/70 computer.

RESULTS AND DISCUSSION

(a) *Regression analysis*: The spectra of BA in different solvents are summarized in table 1. Two main bands appear in 1,4-dioxane solvent having λ_{\max} located at 330 and 255 nm. These two bands may be assigned as being of the $n \rightarrow \pi^*$ type electronic transi-

Table 1 Different solvent parameters and observed λ_{\max} values for BA and TBA.

Solvent	E	M	N	λ_{\max} (nm)	
				BA	TBA
Carbon tetrachloride	32.5	0.22	0.01	310, 258	—
1,4-dioxane	36.0	0.20	0.03	330, 255	335, 287, 240
Acetone	42.2	0.18	0.65	—	330, 297
Dimethyl formamide	43.8	0.20	0.67	310, 268	290, 265
Dimethyl sulphoxide	45.0	0.22	0.66	262	287, 263
Acetonitrile	46.0	0.18	0.71	310, 255	283, 232
Acetic acid	51.1	0.19	0.41	340	287
Ethanol	51.9	0.18	0.67	245	283, 266, 240
Water	63.1	0.17	0.76	248	275, 263, 240

ions. The second band is shifted to shorter wavelengths as the polarity of the solvent increases. The spectra of TBA in different solvents are also reported in table 1. In 1,4-dioxane as solvent three main bands are observed with λ_{\max} located at 335, 287 and 240 nm. As in the case of BA these bands especially the second one are also sensitive to the solvent polarity.

A multiple linear regression analysis has been performed only for the second band of BA and TBA. In each case fits are obtained as a function of the parameter E alone, the parameters E and M , and then the parameters E , M and N . The results are summarized in table 2, where it is clear that the values of the multiple correlation coefficients indicate that the experimental data are best fitted when taking the dependence on the three parameters E , M and N , all together and the parameter E alone is responsible for more than 50% of the fit. This indicates that the shift in peak position on going from a solvent to another is mainly dependent on the solute-solvent hydrogen bonding. The fits also show that the peak position for such polar compounds can be fairly expressed in terms of the solvent polarity parameters E , M and N and confirm the well-known observation that $n \rightarrow \pi^*$ types

electronic transitions are blue-shifted on going from non-polar to polar solvents²³.

(b) *MO calculations*: The PPP calculated electronic transitions together with those observed in 1,4-dioxane as solvent and the estimate for the peak location in the gas phase obtained from the regression analysis are given in table 3. The difference between the PPP calculated values and those observed can be attributed to the different solute-solvent interactions taking place in solution and not considered in the PPP calculations. The agreement was expected to be better with the estimate of the peak position in the gas phase obtained from the regression calculations. However, a good agreement is found in the case of BA but a difference of approximately 1 eV is found in the case of TBA. Of course we are comparing two completely different approaches and the agreement can be fortuitous but both approaches are expected to give the band positions in the gaseous state. The PPP calculated transitions are pure $\pi - \pi^*$ types and are parameters- and geometry-sensitive, while the regression intercept is assumed to be the band position of an electronic transition which has an $n - \pi^*$ character. On the other hand specific solute-solvent interactions particularly

Table 2 The calculated regression coefficients for different fits.

	BA			TBA		
	E only	E and M	E, M and N	E only	E and M	E, M and N
a_0	274.5115	203.6406	232.8592	337.5578	338.7540	334.6818
a_1	-0.4102	-0.0020	-0.6062	-1.1645	-1.4303	-1.2857
a_2	—	267.2670	208.5472	—	69.0812	125.6283
a_3	—	—	19.4363	—	—	-21.2444
MCC*	0.5276	0.6779	0.8254	0.7828	0.8574	0.8805

* Multiple correlation coefficient

Table 3 Different electronic transitions for BA and TBA.

	Electronic transitions ^(a)		
	PPP	Exptl. ^(b)	a_0 ^(c)
BA	4.14	3.76	—
	5.27	4.86	5.3
	6.01	—	—
TBA	3.94	3.70	—
	5.08	4.32	3.7
	5.77	5.17	—

(a) in eV; (b) in 1,4-dioxane as solvent; (c) the regression intercept.

hydrogen bonding as well as non-specific interactions such as dispersion, and dipolar effects expressed in the present model by the parameters M and N taking place in solution are found to play an important role in determining the peak position in different solvents.

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