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Investigation of the Effects of Substituents and Various Solvents on UV-Visible Spectra of 5-(Quinolinylmethylene)barbituric Acid Derivatives

MEVLUDE CANLICA*, H. KERIM BEKER, ALPER AKINCI and SENIZ KABAN
Department of Chemistry, Faculty of Science & Arts, Yildiz Technical University
Davutpasa Campus, Esenler, 34220 Istanbul, Turkey
E-mail: mevludecanlica@gmail.com

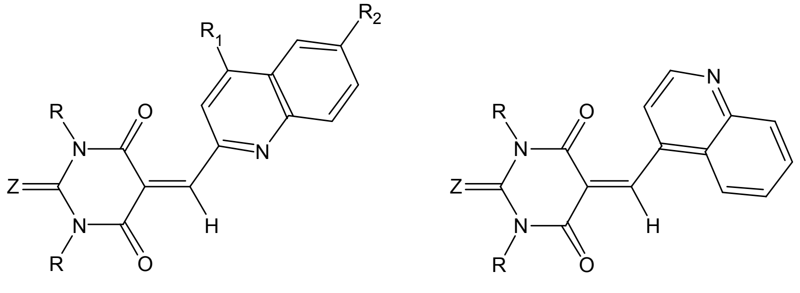
The effects of substituents and solvents on the UV-visible spectra of 5-(quinolinylmethylene)barbituric acid derivatives have been investigated.

Key Words: Barbituric acid, Thiobarbituric acid, Substituent effect, Solvent polarity effect.

INTRODUCTION

Heterocyclic compounds and their derivatives are commonly used in various fields of industry as analytical reagents, ligands, dyestuffs, pharmaceuticals and bioindicators.

In this study, some 5-(quinolinylmethylene)barbituric acid derivatives (**1-6**) were prepared according to the literature procedure[1] and various solvent effects on the absorption spectra of these compounds were investigated (**Scheme-I**). For this reason, solutions of the pure products were prepared as the concentration of 10^{-5} M in $CHCl_3$, THF, MeOH, DMF and DMSO.



(1, 3 - 6) **(2)**

1:	$R = C_2H_5$,	$R_1 = H$,	$R_2 = H$,	Z=S
2:	$R = C_2H_5$,	- ,	- ,	Z=S
3:	$R = C_2H_5$,	$R_1 = H$,	$R_2 = CH_3$,	Z=S
4:	$R = C_2H_5$,	$R_1 = CH_3$,	$R_2 = CH_3$,	Z=S
5:	$R = CH_3$,	$R_1 = H$,	$R_2 = H$,	Z=O
6:	$R = CH_3$,	$R_1 = H$,	$R_2 = CH_3$,	Z=O

Scheme-I

EXPERIMENTAL

Absorption spectra were obtained on an Unicam UV/VIS spectrophotometer. IR spectra were measured with a Shimadzu FTIR 9300 spectrophotometer as potassium bromide pellets. Solvents were distilled prior to reactions.

Compounds **1-6** were dissolved in the solvents that has various polarity such as MeOH, $CHCl_3$, THF, DMF and DMSO. The optimum conditions for concentration were investigated with respect to maximum absorption. Increasing concentration as 10^{-5}, 10^{-4}, 10^{-3} M was lost spectral fine structure when there was hyperchromic effect in absorption spectra. Optimal conditions were chosen as 10^{-5} M, since this gives the highest absorbance value. UV-visible spectra of compound solutions were recorded as freshly (X), one day later (Y) and two months later (Z) against its solvents and then they were compared to each other.

RESULTS AND DISCUSSION

The solutions of the compounds were prepared daily in 10^{-5} M of MeOH, $CHCl_3$, THF, DMF and DMSO. The molar absorption coefficient (ε = mol^{-1} dm^3 cm^{-1}) of solutions were calculated for freshly solvents. The assay results obtained for each solvent and compound are summarized in Table-1.

Investigation of the effect of solvent upon the UV-visible spectra: As shown in Table-1, when the absorption spectra of the compounds were investigated, the same peculiarities were observed to general knowledge. Increasing the polarity of the solvents as DMSO > DMF > MeOH > THF > $CHCl_3$ was generally effected the results in the electronic spectra. Comparison of the UV-visible spectral data clearly supported the formation of the compounds because appearance of various bands at about 241-245, 294-303 and 540 nm were observed in all of the spectra. On the other hand, the absorbance bands were also appeared at 258-278 and 314-321 nm for **5** and **6**.

All compounds showed bathochromic and hypochromic shifts in their spectra at about 240-296 nm by increasing the polarity of the solvents. In $CHCl_3$, **5** and **6** shifted bathochromically to 320 nm while compounds **1-4** gave absorption bands at 241-245 and 296-297 nm. But when the spectra were recorded 1 d later, a new absorption band appeared at 502-549 nm for compounds **3** and **5**. That means, **3** shifted hypsochromically and hyperchromically and **5** shifted hypochromically. After 2 months, the absorption appeared at 486-545 nm and λ_{max} values changed as **1** > **3** > **5**, but **3** gave the highest absorbance value as **3** > **1** > **5**. The UV-visible spectra are given in Figs. 1-3. All the compounds in THF shifted hyperchromically and there were absorption bands at 238-241, 269-271 and 295-297 nm in their spectra. But a new absorbance appeared at 470 nm only for **1**. Compounds in MeOH were shifted bathochromically and hyperchromically, but there was no regular change at 297 nm after 1 d. However, there were the absorption bands at 294-300 nm in DMF for **1-6**. **1** shifted hypsochromically and hypochromically and a new absorbance appeared at 520 nm. Compound **3** shifted bathochromically and hyperchromically and **6** shifted hypochromically. When the DMSO solutions of the compounds were investigated, there was no regular change. Compounds **1** and **3** shifted hypochromically at 298 nm and 306 nm; **2** shifted hypochromically and bathochromically, **5** shifted hypsochromically and hypochromically and **6** shifted hyperchromically. But when the spectra were measured 1 d later, a new absorption band appeared at 486-529 nm for **1**, **3** and **5**.

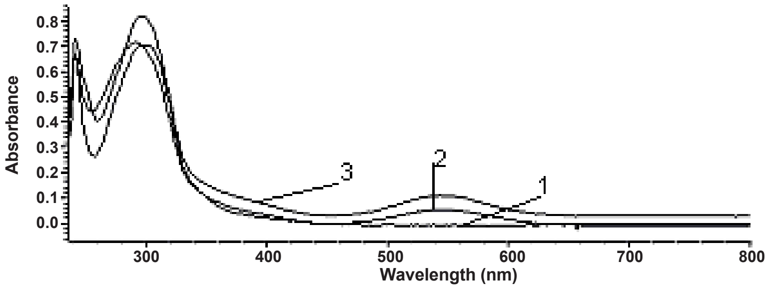


Fig. 1. UV-visible spectra of 10^{-5} M compound **1** in $CHCl_3$, as 1: X, 2: Y, 3: Z

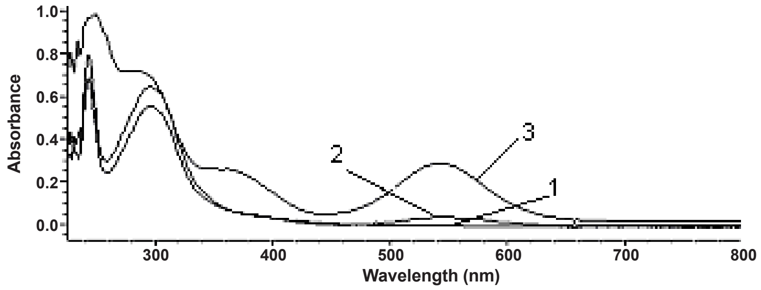


Fig. 2. UV-visible spectra of 10^{-5} M compound **3** in $CHCl_3$, as 1: X, 2: Y, 3: Z

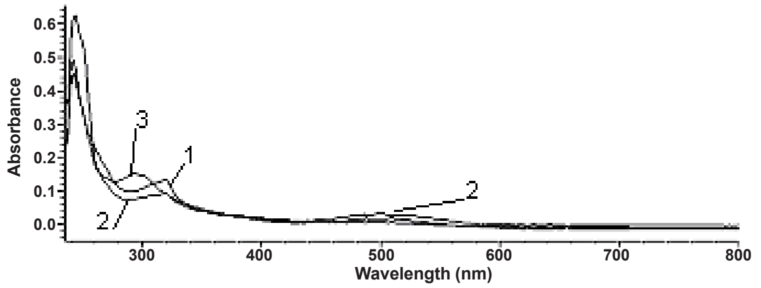


Fig. 3. UV-visible spectra of 10^{-5} M compound **4** in $CHCl_3$, as 1: X, 2: Y, 3: Z

Effect of substituents upon the UV-visible spectra: Compound **1** shifted hyperchromically with increasing time and a new absorption band appeared at 545 nm in $CHCl_3$. This situation can be explained by longer conjugated system which gives a tautomeric equilbrium. Because, $CHCl_3$ is a H^+ donating solvent and these protons can be attached to -C=O groups in the structures. Thus occured hydroxy groups are also electron donating and electrons can be given to the barbituric acid ring system[2]. Supporting to these results, 2 months solutions were evaporated almost to dryness and then their IR spectra were taken by using KBr pellets. A new absorption band corresponding to -OH group was observed at around 3445 cm^{-1} which is not present in the IR spectra of the solid compounds.This can be explained by the formation of strong intra molecular H-bonds. Apperance of this band confirmed the data obtained by UV-visible spectrophotometric method. There was no absorption at about 500 nm for compound **1** in MeOH solution. This can be defined by the highest acceptor number of methanol according to other solvents. As mentioned above, $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions of compound **1** shifted hyperchromically in $CHCl_3$ due to the highest ionic influence of this solvent and THF also showed the same results.

When the freshly measured spectra of compound **2** in all used solvents were compared to each other, they showed only hyperchromic shift. But, additional hypochromic and bathochromic shifts were observed in the spectra of compound **2** taken one day later and two months later. This situation is possibly related with the changing of the position of N in structures, although compounds **1** and **2** have the same molecular weight.

These results were also supported by the spectral data of compound **3** which has one methyl group at the 6-position of quinolinyl ring. In spite of this, compound **4** which has two methyl groups (at 4- and 6-positions of quinolinyl ring), have a hyperchromic shift for $\pi\rightarrow\pi^*$ transition as well as a hypochromic shift for $n\rightarrow\pi^*$ transition and absence of a band at about 500 nm due to the additional methyl group. This effect was confirmed by the structue of compound **1** and was also supported by the spectral data of compound **5**. However, there is -C=O group instead of -C=S in the structure of compound **5** and presence of this group can explain the hypochromic shift at 500 nm.

When compound **6** was taken into consideration, hypochromic shifts for $\pi\rightarrow\pi^*$ transitions were observed related with the increasing solvent polarity and time and there was no band at about 500 nm in the spectra. This shift was probably occured *via* effect of -C=O group and 6-methyl group in the quinoline ring.

There are B bands in the spectra of all compounds as shown in **Scheme-I**. Increasing of the conjugation in the systems bathochromically shifted the λ_{max} to the longest wavelength. This can be supported by occuring a new absorption at about 500 nm.

On the other hand, it was also investigated whether or not there is the effect of UV radiation and soluble oxygene upon the resulting spectra. Therefore, 10^{-5} M solution of compound **1** in $CHCl_3$ was prepared and then separated into 4 parts (Part 1-4). These solutions were subjected to the different conditions such as argon atmosphere (Sample 1), both argon atmosphere and UV radiation for 6 h (Sample 2), UV radiation for 6 h (Sample 3), working conditions (daylight at room temperature)

TABLE-1
UV-VISIBLE SPECTRAL DATA OF 10^{-5} M COMPOUNDS IN VARIOUS SOLVENTS

Compd.	Solvent		Fresh (X)				One day (Y)				Two months (Z)			
1	$CHCl_3$ (1)	λ	241	297	398		241	291		546	241	296		545
		A	0.666	0.704	-		0.670	0.714		-	0.730	0.820		0.110
		log ε	4.35	4.37										
	THF (2)	λ	238	270	295	430	238	267	295	488	239	267	294	470
		A	0.582	0.378	0.64	-	0.526	0.381	0.602	-	0.739	0.575	0.614	0.063
		log ε	3.38	4.10	4.23									
	MeOH (3)	λ		297		485	268	-	399			308	369*	
		A		0.348		-	1.918	-	0.052			0.986	0.287	
		log ε		4.06										
	DMF (4)	λ		267	302			267	297				293	520
		A		0.444	0.463			0.430	0.461				0.391	0.012
		log ε		4.17	4.19									
	DMSO (5)	λ		277	306			276	304	526	260		305	525
		A		0.425	0.488			0.480	0.474	0.091	0.340		0.360	0.310
		log ε		4.15	4.21									
2	$CHCl_3$ (1)	λ	239	271	297		239	275	293		-	271	291	
		A	0.276	0.209	0.346		0.218	0.288	0.327		-	0.036	0.166	
		log ε	4.26	4.14	4.36									
	DMF (4)	λ			294				293				295	
		A			0.374				0.667				0.675	
		log ε			4.40									
	DMSO (5)	λ			298				298	254		271*	304	
		A			0.293				0.322	0.263		0.241	0.298	
		log ε			4.33									
3	$CHCl_3$ (1)	λ	243		296		243		295	549	249	274	369*	543
		A	0.795		0.642		0.684		0.60	0.034	0.981	0.721	0.220	0.286
		log ε	4.75		4.66									
	THF (2)	λ	241	269	297		240	270	295		241	270*	294	
		A	0.606	0.290	0.499		0.564	0.289	0.340		2.334	0.745	0.759	
		log ε	4.64	4.32	4.55									
	DMF (4)	λ		267	296			267	296				301	
		A		0.411	0.439			0.392	0.450				0.502	
		log ε		4.47	4.50									
	DMSO (5)	λ		278	298		277	304		529	260	301	374*	525
		A		0.452	0.470		0.433	0.460		0.022	0.542	0.456	0.152	0.240
		log ε		4.51	4.52									

4	$CHCl_3$ (1)	λ	245	303		244	302			245	257*	304	
		A	0.682	0.329		0.602	0.311			0.470	0.381	0.367	
		log ε	4.69	4.37									
5	$CHCl_3$ (1)	λ	242		320	242	320		502	243	293		502
		A	0.489		0.134	0.43	0.094		0.032	0.624	0.152		0.006
		log ε	4.59		3.90								
	DMSO (5)	λ	258		321	260	320		486	258	291		486
		A	0.139		0.063	0.200	-		0.030	0.293	0.130		0.078
		log ε	2.93		3.57								
6	$CHCl_3$ (1)	λ	244		320	242		313		256		311	
		A	0.572		0.134	0.320		0.121		0.357		0.124	
		log ε	4.55		3.92								
	DMF (4)	λ	266		297	267		301		268		300	
		A	0.246		0.490	0.097		0.086		0.045		0.071	
		log ε	3.07		3.06								
	DMSO (5)	λ	260	310*	314*	260		312*		258		312*	
		A	0.118	0.015	0.014	0.247		0.093		0.181		0.075	
		log ε	3.87	2.97	2.94								

*Shoulder.

TABLE-2
UV-VISIBLE SPECTRAL DATA OF 1.5 × 10^{-5} M COMPOUND **1** IN $CHCl_3$

Compound **1**		Part 1-4, Fresh (X)		Fresh, operation later (X')			One day (Y)			Three months (T)		
1 (Ar)	λ	241	298	241	297		241	296		242	302	546
	A	0.230	0.309	0.230	0.313		0.230	0.341		0.441	0.288	0.030
2(Ar,UV)	λ	241	297	242	299	542	242	298	542	242	303	
	A	0.237	0.308	0.260	0.266	0.044	0.311	0.282	0.072	0.454	0.259	
3 (UV)	λ	241	298	242	302		242	300		242	303	
	A	0.233	0.303	0.248	0.252		0.287	0.266		0.438	0.237	
4 (-)	λ	241	297	241	297		241	296		242	303	
	A	0.281	0.342	0.262	0.346		0.328	0.371		0.478	0.360	
5 (Solid) (3.0 × 10^{-5})	λ	241	296				241	295	545	242	300	
	A	0.529	0.614				0.603	0.612	0.062	1.005	0.647	

(Sample 4), respectively. In addition, crystals of compound **1** were kept at working conditions for 3 months (Sample 5). UV-visible spectra of Part 1-4 as freshly (X) and then, Sample 1-5 solutions were recorded immediately after operation (X'), one day later (Y) and three months later (T) against the solvent as blank solution. When the obtained spectra were investigated hyperchromic, bathochromic and hypochromic shifts were observed. A new absorption band was appeared at about 546 nm in the spectra of Sample 2 and Sample 5 (Y). The obtained results for each conditions are summarized in Table-2. These results showed that the UV radiation and soluble oxygene can effect upon the UV-visible spectra of the compound. The results obtained from Sample 1 showed the effect of soluble oxygene. However, UV radiation was more effective when the experiments done in argon atmosphere (Sample 2). Thus, it is clear from these results that the solvent has the major effect on the UV-visible spectra of the compounds. In addition to these, there was a new absorption band two months later (Z), but three months later (T), this band disappeared. This datum may be explain by the decomposition of the compound.

As a consequence, UV-visible spectral data are in accordance with the structures and clearly indicated tautomeric equilibrium.

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