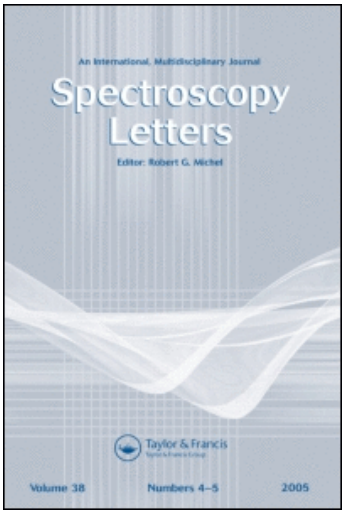

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SPECTROSCOPIC STUDY OF TAUTOMERISM IN 2-BENZOYL-4-PHENACYL-1,3-CYCLOPENTANEDIONE

Key words: UV-VIS spectrophotometry, First derivative spectrophotometry, Tautomerism, 2-Benzoyl-4-phenacyl-1,3-cyclopentanedione.

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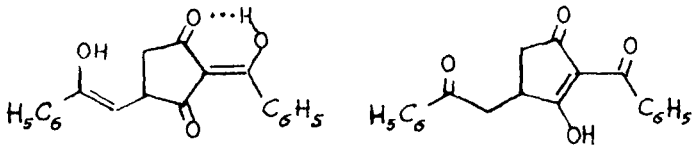
ABSTRACT

The tautomerism in 2-benzoyl-4-phenacyl-1,3-cyclopentanedione has been studied through an investigation of the solvent and pH dependence of the equilibrium using UV spectrophotometry. The first derivative spectrophotometric technique has been applied for the determination of the ratio of monoenol form in tautomeric mixtures. The results showed that in DMF solution 2-benzoyl-4-phenacyl-1,3-cyclopentane-dione exist only in non-hydrogen-bonded monoenol form while in less polar solvents the predominance of helated dienol form was established.



Scheme 1

INTRODUCTION

2-Benzoyl-4-phenacyl-1,3-cyclopentanedione prepared by the condensation of acetophenone and diethyl maleate using an excess of sodium ethoxide can exist in a solid state as two stable tautomers. On the basis of spectral analysis it has been suggested that isomer 1 (Scheme 1) is completely enolised forming a conjugated chelate system (dienol) and that isomer 2 is enolised preferentially in the five-membered ring (monoenol)[1].

It has been observed that by recrystallization of compound 1 from MeOH or glacial acetic acid a certain quantity of compound 2 is always obtained from mother liquor. Moreover, enolic tautomer 1 can be easily converted to its isomer 2 by heating or during longer standing of its dilute acid solutions at room temperature.

The keto-enol tautomerism of β-tricarbonyl compounds has been the subject of a very large number of studies[2-6], but no investigations have been reported on the tautomerism of the 2-benzoyl-4-phenacyl-1,3-cyclopentandione system.

The aim of this work is to study the solvent effect and influence of pH on tautomerism in 2-benzoyl-4-phenacyl-1,3-cyclopentandione as well as the application of derivative spectrophotometry to the quantitation of enolic forms in tautomeric equilibrium mixture.

EXPERIMENTAL

Apparatus

For recording of UV spectra and its first derivatives Varian DMS 80 UV-Vis spectrophotometer was used. Measurement settings were: scan range 190-400 nm; scan speed 100 nm min^{-1}; chart speed 100 mm min^{-1}; ordinate maxima and minima ± 0.2; slit width 2 nm.

Materials

Compound 1, [2-(1-hydroxy-1-phenylmethylene)-4-(2-hydroxy-2-phenylethenyl)-cyclopentane-1,3-dione], and compound 2, [2-benzoyl-4-phenacyl-3-hydroxycyclopent-2-ene-1-one],were prepared according to the method described in privious paper.[1] All solvents were of analytical grade (Merck). Solutions were buffered by citrate buffer pH = 5 and 6 (Kemika).

Procedure

Stock solution of compound 2, γ = 36 μg ml^{-1}, was prepared by dissolving accurately weighted amount of substance in 50 ml of chloroform. All other stock solutions of compound 2 in different solvents were prepared in the same way. Calibration graphs were obtained by measuring the peak amplitude at 288 nm of the first derivative absorption spectra obtained by recording zero order absorption spectra (UV spectra) of different aliquots of stock solutions in different solvents. The percentage of isomer 2(compound 2) was calculated from the peak amplitude at 288 nm obtained by recording the first derivative spectra of compound 1 and calibration graphs.

RESULTS AND DISCUSSION

Absorption spectra of compound 1 dissolved in different solvents (selection limited by the poor solubility in non-

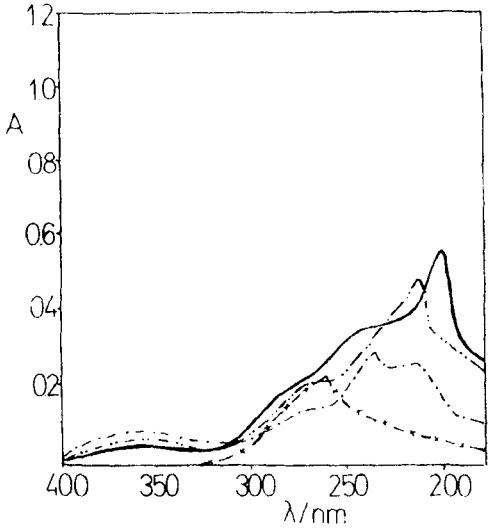


Fig. 1. Solvent effect on absorption spectra of compound 1 γ(compound 1)/μg ml^{-1}: 11.9 in CH_3Cl (—·—); 14.4 in EtOH (———); 14.9 in CH_3CN (—··—); 13.8 in DMF (—×—)

polar solvents) show four absorption bands with absorption maxima and the respective intensities differing from solvent to solvent (FIG. 1 and Table 1).

The spectra of compound 2 exhibit the similar pattern of absorption, only the absorption maxima in the 300-360 nm region is missing (FIG. 2 and Table 1). This implies that UV spectra of compound 1 give a good indication of the extent of enolization in different solvents.

By dissolution in DMF compound 1 is converted to its isomer, monoenol form, being proved by identical UV spectra (FIGS. 1 and 2 and Table 1). In $CHCl_3$, CH_3CN and EtOH both tautomeric forms are present (isomer 1 and 2).

On the other hand the absorbance data indicate that compound 2 in all examined solvents is completely in monoenol form (FIG. 2 and Table 1).

TABLE 1.

Effect of Solvents on the Absorption Spectra of Isomers 1 and 2 of 2-Benzoyl-4-Phenacyl-1.3-Cyclopentanedione

		Isomer			
		Equilibrium mixture		Monoenol	
Comp.	Solv.	λ/nm	lg[ε/(M^{-1} cm^{-1})]	λ/nm	lg[ε/(M^{-1} cm^{-1})]
1	CH_3Cl	213	4.34		
		233	4.40		
		266sh	4.07		
		352	3.83		
	EtOH	198	4.60		
		224	4.40		
		265sh	4.22		
		360	3.44		
	CH_3CN	210	4.51		
		222sh	4.40		
		263sh	4.16		
		354	3.64		
	DMF			262	4.25
2	$CHCl_3$			212sh	4.31
				234	4.41
				250	4.46
				266sh	4.31
	EtOH			198	4.54
				242	4.38
				264sh	4.18
	CH_3CN			210	4.30
				242	4.30
				263sh	4.17
	DMF			262	4.25

The proportions of tautomers in different solvents were estimated by assuming that the absorbance of the 250-280 nm band is entirely due to the benzoyl and phenyl vinyl ketone structure of monoenol form (isomer 2) and that the absorbance of the 300-360 nm band is due to cinnamoyl chromophore of dienol form (isomer 1)[7].

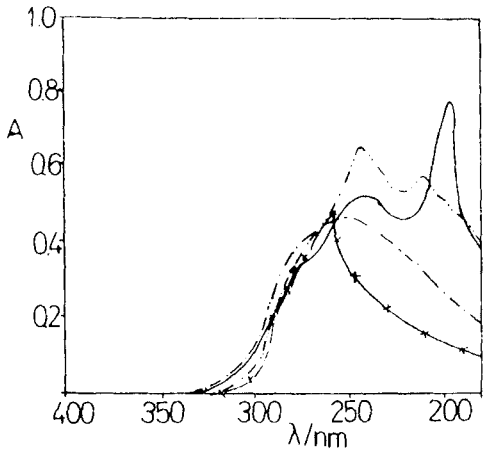


Fig. 2. Solvent effect on absorption spectra of compound 2 γ(compound 2)/μg ml^{-1}: 16.6 in CH_3Cl (—·—); 22.5 in EtOH (——); 30.0 in CH_3CN (—··—); 27.5 in DMF (—×—)

The absorbance spectra of compound 2 (monoenol form) do not exhibit sharp maxima in 250-300 nm region which can be used for reliable direct absorbance measurements. These difficulties were overcome by the use of first derivative spectrophotometry[8,9]. FIG. 3 shows the absorption (zero order) spectra of compounds 1 and 2 recorded in chloroform while FIG. 4 is their first derivative spectra, where compound 2 shows two well-defined peaks in examined region. These two well-defined peaks have been obtained in first derivative spectra of compounds 1 and 2 recorded in acetone and acetonitrile too.

By applying the first derivative technique, a linear correlation was obtained between the peak amplitude at 288 nm and concentration of compound 2 over the range γ = 3.6-10.8 μg ml^{-1} (in chloroform), γ = 3.8-8.6 μg ml^{-1} in ethanol) and γ = 3.8-9.6 μg ml^{-1} (in acetonitrile). The regres-

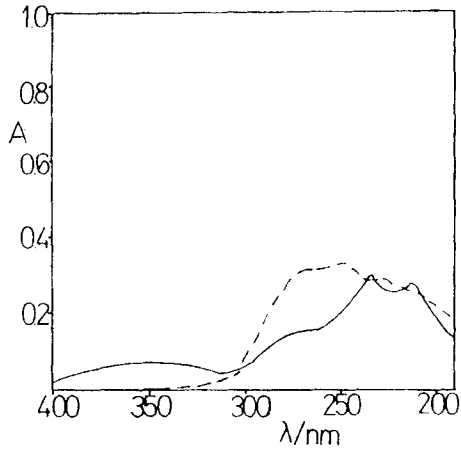


Fig. 3. Zero order absorption spectra in CH_3Cl of:
(——) γ(compound 1) = 11.9 μg ml^{-1}
(- - -) γ(compound 2) = 15.7 μg ml^{-1}

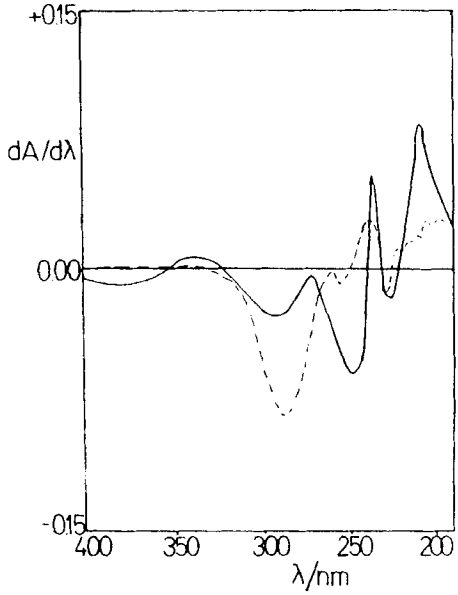


Fig. 4. First derivative spectra in CH_3Cl of:
(——) γ(compound 1) = 11.9 μg ml^{-1}
(- - -) γ(compound 2) = 15.9 μg ml^{-1}

TABLE 2.

Parameters of Calibration Graphs Used for the Determination of Compound 2 in Different Solvents for n=4

Solvent	Regression equation	Correlation coefficient r	Variance s^2
$CHCl_3$	D1=-0.0103+0.071c	0.9997	$2.3 \cdot 10^{-6}$
EtOH	D1= 0.0043+0.037c	0.9998	$2.0 \cdot 10^{-7}$
CH_3CN	D1=-0.0044+0.043c	0.9963	$2.6 \cdot 10^{-5}$

TABLE 3.

Percentage of Isomer 2 in Different Solvents Determined after 30 min by the First Derivative Spectrophotometry

	Solid[1]	Solvents			
		$CHCl_3$	EtOH	CH_3CN	DMF
w(Isomer)/%	100.0	25.3	75.0	72.0	100.0

sion linear equations for compound 2 in examined solvents are shown in Table 2, together with correlation coefficients, r, and variance, s^2.

By use of this equations it is possible to determine compound 2 selectively in the presence of compound 1 in equilibrium mixtures.

The content of monoenol form (compound 2) increases by changing the solvent from chloroform to DMF suggesting that the ratio of isomer 2 is enhanced through solvent polarity.

The reverse is true for ethanol were the tautomerism is enhanced through hydrogen-bond mechanism where the solvent acts as a hydrogen donor and acceptor (Table 3).

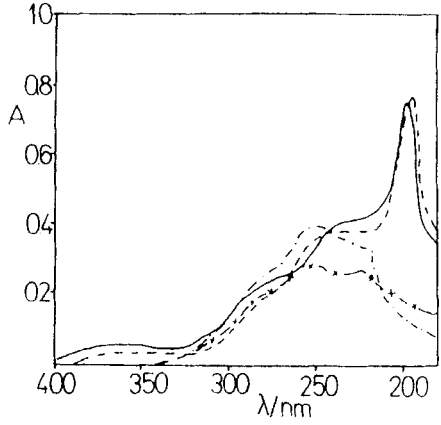


Fig. 5. Influence of pH on absorption spectra of compound 1 in EtOH γ(compound 1) = 21.9 μg ml^{-1}; (– – –) c(HCl)=0.1 M; (—·—) c(NaOH)=0.1 M; (—x—) pH=6 (citrate buffer)

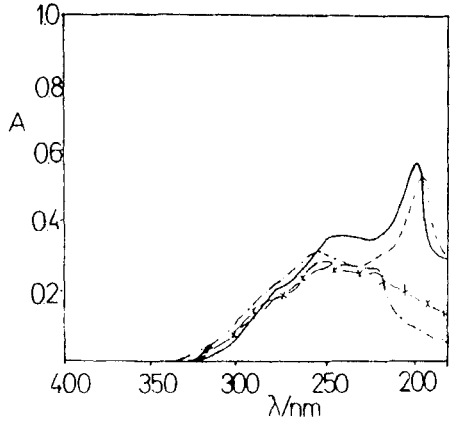
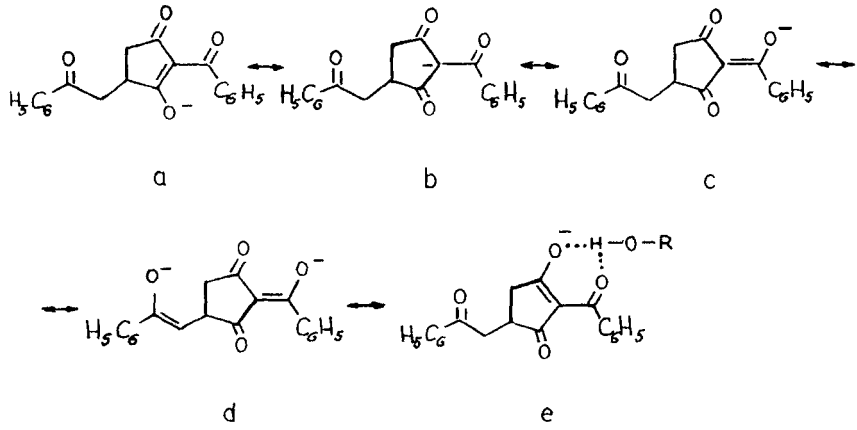


Fig. 6. Influence of pH on absorption spectra of compound 2 in EtOH γ(compound 2) = 13.5 μg ml^{-1}; (– – –) c(HCl)=0.1 M; (—·—) c(NaOH)=0.1 M; (—x—) pH=6 (citrate buffer)

The effect of pH on the absorption maxima of compound 1 and 2 have been studied too (FIGS. 5 and 6). For both compounds the UV spectra in comparison with spectra recorded in ethanol show bathochromic shift of the absorption maxima in alkaline solutions, demonstrating that enolic function is a part of a highly conjugated chromophore. In alkaline solutions enol can probably exist in several forms such as:



Scheme 2

Ionic form "d" may exist as a "solvent chelate" complex in hydroxylic solvents[10]. When the ethanolic solutions of both compounds are buffered at pH = 5 and 6 (citrate buffer) the intensities of absorption maxima are slightly lower.

In more acidic solutions, c(HCl) = 0.1 M, absorption maxima of compounds 1 and 2 show the hypsochromic shift and the spectra are very similar to those in ethanol. The absorption spectrum of compound 1 in acidic media shows that a certain quantity of dienol form is still present (FIG. 5). On longer standing dienol form (isomer 1) converts completely to monoenol form (isomer 2). The studies on the kinetics of enolization are in progress.

REFERENCES

1. Lazarević Z., Vorkapić-Furač J., Mühl J. β-Tricarbonyl Compounds. I. 2,4-Disubstituted 1,3-Cyclopentanediones. Monatsh. Chem. 1992; (in press).
2. Merenyi F., Nilsson M. Spectroscopic Studies on Enols. Part 7. NMR and IR Investigations of Hydrogen Bonding and Tautomerism in Cyclopentane Enols. Acta Chem. Scand. 1967; 18: 1208.
3. Forsen S., Merenyi F., Nilsson M. Spectroscopic Studies on Enols. Part 8. Preferential Ring Enolization of 2-Formylcyclopentane-1,3-dione. Acta Chem. Scand. 1967; 21: 620.
4. Gren E.J., Zelmen V.N., Grinvalde A.K., Vanag G.J. Stroenie i IKS 2-acilindendionov-1,3. Izv. Akad. Nauk Latv. SSR, Ser. Khim. 1965; 593.
5. Forsen S., Nilsson M., Elvidge J.A., Burton J. S., Stevens R. Spectroscopic Studies on Enols. Part 6. Enolization and Hydrogen Bonding in 3-Acylcyclopentane-1,2,4-triones. Acta Chem. Scand. 1964; 18: 513.
6. Avakyan V.G., Gromak V.V., Kurbako V.Z. Kvantno-himičeskoe issledovanie tautomeriji 2-acetilciklopentan-1,3-diona. Izv. Akad. Nauk SSSR, Ser. Khim. 1989; 2377.
7. Campbell R.D., Gilow H.M. β-Diketones. II. Ultraviolet and Infrared Spectra of some 2-Aroylcyclohexanones. J. Am. Chem. Soc. 1960; 82: 5426.
8. Shibata S., Furukawa M., Goto K. Dual-Wavelength Spectrophotometry Part IV. Qualitative and Quantitative Analysis by Means of First-Derivative Spectra. Anal. Chim. Acta 1973; 65: 49.
9. Wahbi A. M., Ebel S. The Use of the First-Derivative Curves of Absorption Spectra in Quantitative Analysis. Anal. Chim. Acta 1974; 70: 57.

10. Chan W. R., Hassall C.H. 2-Acyl Derivatives of Cyclic 1:3-Diones. Part III. Ultraviolet and Infrared Absorption Spectra of 2-Acylcyclohexane-1:3-Diones. J. Chem Soc. 1956; 3495.

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