ELSEVIER

Photoinduced ketonization of poly(ethylacrolylacetate) in solution

Ivan Petkov[a], Nadejda Sertova[a], Ljudmil Grigorov[a], Seizo Masuda[b]

[a]*University of Sofia, Department of Organic Chemistry, 1 James Bourchier Avenue, 1126 Sofia, Bulgaria*
[b]*Department of Applied Chemistry, Technical College, The University of Tokushima, Tokushima 770, Japan*

Abstract

The influence of UV irradiation on the keto to enol ratio of poly(ethylacrolylacetate) (PEAA) in solution was examined. The major process is photoketonization, which is rapid and reversible. The role of the polymer chain is discussed in terms of its effect on the phototransformation. It is suggested that the high rate of photoketonization may be associated with the formation of sandwich complexes between the different units.

Keywords: Ketonization

1. Introduction

In previous papers [1–4], the effect of UV irradiation on β-dicarbonyl compounds (β-DCCs) has been discussed. A number of investigations have presented evidence to indicate that, at least in the specific systems studied, photoinduced ketonization proceeds by the formation of an unstable, non-chelated rotamer of the enol form [5,6]. Twisting around the carbon–carbon double bond is possible in the excited state of the molecule.

This paper presents a study of the photoinduced ketonization of poly(ethylacrolylacetate) (PEAA). The choice of PEAA was based on the hope that the peculiar structure of the polymeric β-DCC may influence the process of ketonization. The presence of a polymeric chain in PEAA may limit the rate of proton motion which is an important type of reaction in organic chemistry and biochemistry. The present study was undertaken to gain further insight into the influence of structural features on the process of photoketonization.

2. Experimental details

PEAA was produced by the process of Masuda et al. [7]. Solvents (spectroscopic grade, Fluka) were used as received.

The samples (2 ml of solutions) were thermostatically controlled at 20 °C in a quartz glass vessel and exposed to monochromatic (254 nm) UV irradiation under standard conditions. The photochemical experiments were carried out using a medium-pressure mercury vapour lamp (Narva) as light source in combination with the required filters. The quantum yields were determined using uranyl oxalate as actinometer by applying the procedure described in Ref. [8] taking $\phi = 0.60$ at 254 nm. The irradiation intensity received by the reaction solution was measured to be 1.29×10^{-16} quanta s^{-1} cm^{-3}.

The UV absorption spectra were measured on a Specord UV–visible spectrophotometer. The IR spectra were measured on a Specord 75 IR spectrophotometer. The nuclear magnetic resonance (NMR) spectra were recorded on a Tesla BS 487C 80 MHz spectrometer. Tetramethylsilane was used as the internal standard.

3. Results

The UV spectra of PEAA in different solvents show an intense band in the 245–260 nm region. According to Morton et al. [9], the high-intensity band is associated with the π–π^* transition in the carbonyl-conjugated ethylene fragment (enol form). The type of solvent does not influence the position of the band. The keto to enol ratio of the β-dicarbonyl unit in PEAA is not always equal to that of the monomeric β-DCC. The enol fraction in the polymer was measured using an NMR spectrometer and found to be 34% (in $CDCl_3$). It is approximately equal in different solvents [10].

Table 1
Spectral characteristics of PEAA

UV data		^{1}H NMR data		
Solvent	λ_{max} (nm)	Group	δ (ppm)	(Lit) [7]
CH_2Cl_2	247	$=CH-$	4.98	(5.1)
$(CH_2)_2Cl_2$	250	$-CH_2-$	3.51	(3.6)
$CHCl_3$	250	$-OH$	12.12	Unclear
CH_3CN	250	–	–	–
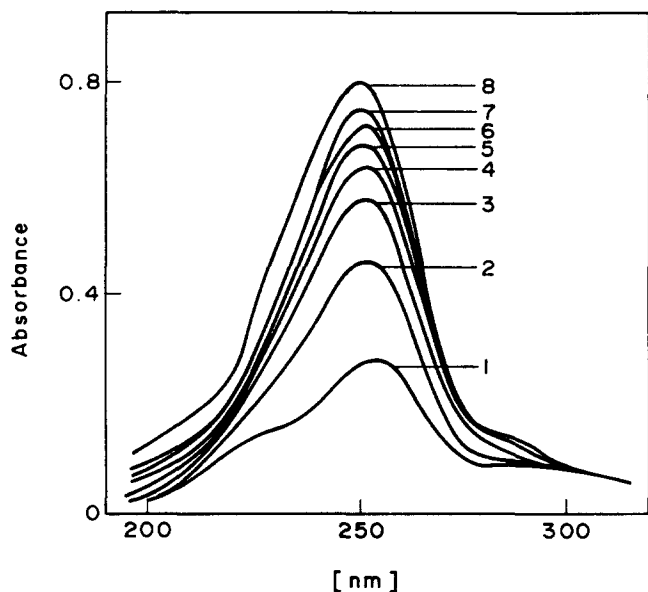
Fig. 1. UV spectra of PEAA in $(CH_2)_2Cl_2$ $(C=1\times10^{-4}\,g\,l^{-1})$ measured at different times (during 15 s) after the start of irradiation (254 nm): 1, unirradiated; 2–8, irradiated.

The absorption bands at about 1725 cm^{-1} (diketo) and 1600 cm^{-1} (enol) in the IR spectra of PEAA correlate with the NMR and UV data (Table 1). The equilibrium proportion between the keto and enol forms in PEAA is similar to that of acetoacetic ester under the same conditions [11]. The *cis*-chelate form is dominant. There is no direct evidence for the presence of the *trans*-enol form.

3.1. Photochemical experiment

The changes in the UV spectra of PEAA on exposure to UV light are shown in Fig. 1. The absorption maximum at 250 nm (enol form) disappears on irradiation. There is a process of rapid restoration after irradiation to the initial keto to enol ratio (Fig. 2). It is important to note that only in CH_3CN is the formation of a weak band at 220–230 nm observed. However, after irradiation, the peak at 250 nm (*cis*-enol form) is restored. In the IR spectrum the bands at 1725 and 1705 cm^{-1}
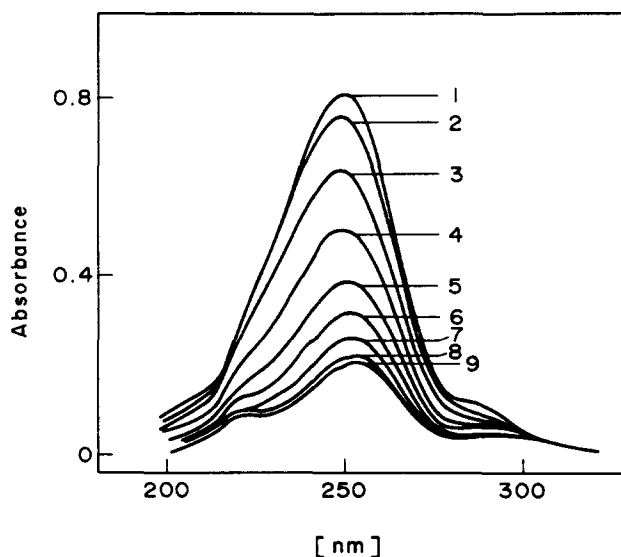

Fig. 2. UV spectra of PEAA in $(CH_2)_2Cl_2$ $(C=1\times10^{-4}\,g\,l^{-1})$ measured at different times (during 10 min) after the cessation of irradiation (254 nm).
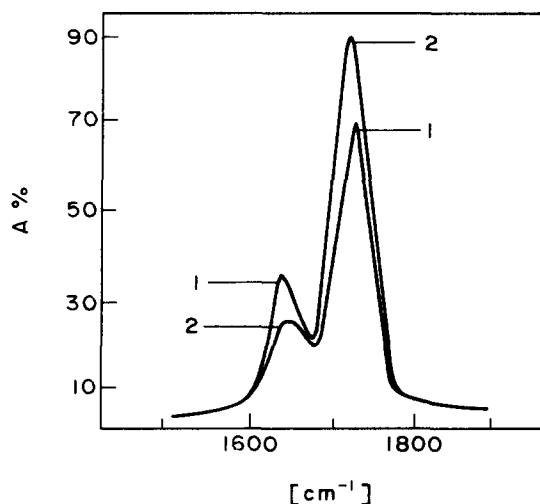

Fig. 3. Changes in the IR spectrum of PEAA in $CHCl_3$ $(C=1\times10^{-2}$ g $l^{-1})$: 1, unirradiated; 2, irradiated.

(the carbonyl field) increase and that at 1595 cm^{-1} decreases on exposure to UV light (Fig. 3).

3.2. Kinetic experiments

The reaction kinetics of the photoinduced transformation of PEAA are complex. The changes in absorbance of the solutions of PEAA on UV light irradiation are presented in Table 2.

A kinetic model considering the presence or absence of the *trans*-enol form was applied to PEAA and a simulation is presented to explain the photoreaction

Table 2
Observed changes in the absorbance of solutions of PEAA during UV light irradiation

| τ_{irr} (s)	Fresh solution	Stable solution
0	0.73 ± 0.015	0.57 ± 0.02
15	0.67 ± 0.025	0.50 ± 0.03
30	0.61 ± 0.02	0.44 ± 0.03
45	0.56 ± 0.02	0.39 ± 0.03
60	0.51 ± 0.02	0.34 ± 0.03
75	0.47 ± 0.025	0.32 ± 0.03
90	0.43 ± 0.025	0.29 ± 0.03
105	0.41 ± 0.02	0.28 ± 0.03
120	0.38 ± 0.025	0.26 ± 0.03

of *cis*-enol to the diketo form and its dependence on the photoisomerization of *cis*-enol to *trans*-enol. In the equations, the concentrations of *cis*-enol (C_e), *trans*-enol (C_t) and the diketo form (C_k) present in latent form are in accordance with the Beer–Lambert law

$$A = \epsilon c l$$

where A is the absorption of the *cis*-enol form, ϵ is the molar extinction coefficient, c is the concentration of the absorbing form and l is the path length of the solution.

3.2.1. A kinetic model with the participation of the trans-enol form

The scheme below shows the kinetic model considering the presence of the *trans*-enol form
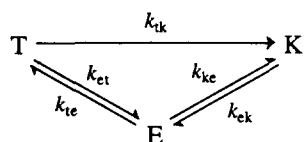
where E is the *cis*-enol form, K is the diketo form and T is the *trans*-enol form.

This model can be represented by a system of first-order differential equations

$$\frac{dC_e}{dt} = -(k_{et} + k_{ek})C_e + k_{te}C_t + k_{ke}C_k$$

$$\frac{dC_t}{dt} = k_{et}C_e - (k_{te} + k_{tk})C_t$$

$$\frac{dC_k}{dt} = k_{ek}C_e + k_{tk}C_t - k_{ke}C_k$$

for the following condition

$$C_e + C_t + C_k = C_0$$

where C_0 is the total concentration, C_e is the concentration of *cis*-enol, C_t is the concentration of *trans*-enol,

C_k is the concentration of the diketo form and k_{ij} are the corresponding kinetic constants. This condition expresses the law of the preservation of substance. In our case, the system is special (the equations are dependent on the experimental conditions), and the solution of the system can be presented in the form

$$C_e = C_{e,0} - A_t[1 - \exp(-a_t t)] - A_k[1 - \exp(-a_k t)]$$

$$C_t = C_{t,0} + A_t[1 - \exp(-a_t t)] \qquad (1)$$

$$C_k = C_{k,0} + A_k[1 - \exp(-a_k t)]$$

where

$$a_t = k_{te} + k_{et} + k_{ek}$$

$$a_k = k_{te} + k_{ke} + k_{ek}$$

$$A_t = C_0 \left(\frac{C_{t,0}}{C_0} + \frac{k_{ke}k_{et}}{B_{tt}B_{kk} + k_{et}B_{kt}} \right)$$

$$A_k = C_0 \left(\frac{C_{k,0}}{C_0} + \frac{B_{tt}k_{ek} + B_{kt}k_{et}}{B_{tt}B_{kk} + k_{et}B_{kt}} \right)$$

and

$$B_{tt} = k_{te} + k_{et} + k_{tk}$$

$$B_{kk} = k_{ke} + k_{ek}$$

$$B_{kt} = k_{tk} + k_{ek}$$

The experimental results (Table 2) were fitted using Eq. (1). The observed data are presented in Table 3. The small differences between the values of A_t and A_k and a_k and a_t for each example and the fact that A_t and A_k have opposite signs show that this model is not applicable (one the exponents in Eq. (1) could be omitted).

3.2.2. A kinetic model with the absence of the trans-enol form

The scheme below shows the kinetic model considering the absence of the *trans*-enol form
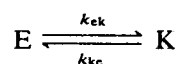
The kinetic model can be represented by the equations

Table 3
Results of the fitting of the experimental data using the kinetic model with the participation of the *trans*-enol form

Sample	C_0	A_t	a_t	A_k	a_k
Fresh solution	0.72	24.75	0.0195	−24.31	0.0197
Stable solution	0.57	24.57	0.0287	−24.23	0.0289

Table 4
Results of the fitting of the experimental data using the kinetic model with the absence of the *trans*-enol form

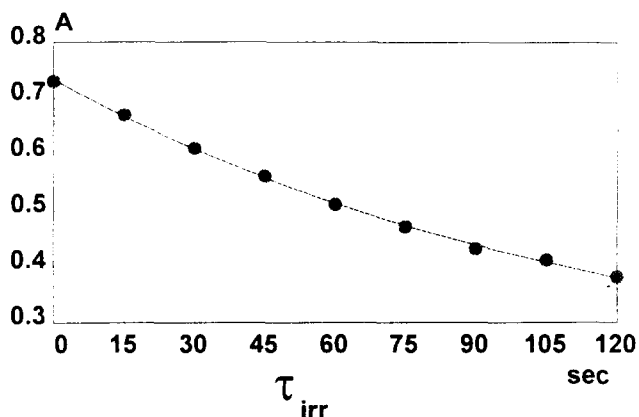| Sample	C_0	A_k	a_k	R^2
Fresh solution	0.73	0.556	0.00845	0.99913
Stable solution	0.57	0.374	0.01526	0.99812

Fig. 4. Results of the fitting of the experimental data using the kinetic model with the absence of the *trans*-enol form.
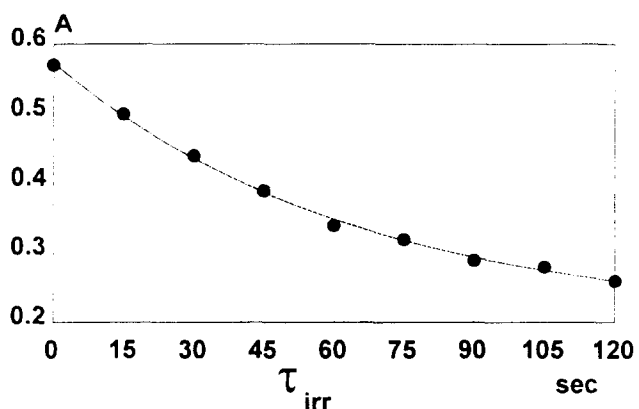

Fig. 5. Results of the fitting of the experimental data using the kinetic model with the absence of the *trans*-enol form.

$$\frac{dC_e}{dt} = -k_{ek}C_e + k_{ke}C_k$$

$$\frac{dC_k}{dt} = k_{ek}C_e - k_{ke}C_k$$

where k_{ij} are the corresponding kinetic constants. Because of the conditions

$$C_e + C_k = C_0$$

$C_0 = $ constant

the solution can be expressed as

$$C_e = C_{e,0} - A_k[1 - \exp(-a_k t)]$$

$$C_k = C_{k,0} + A_k[1 - \exp(-a_k t)]$$

where

$$a_k = k_{ke} + k_{ek}$$

$$A_k = C_0\left(\frac{k_{ek}}{k_{ke} + k_{ek}} - \frac{C_{k,0}}{C_0}\right)$$

The results of the experimental data fitting are presented in Table 4 and Figs. 4 and 5. The large values of the correlation coefficient R support the validity of this model.

4. Discussion

The experimental data indicate that, in PEAA on exposure to UV light, ketonization occurs. In the monomeric β-DCC, irradiation in the spectral region in which the *cis*-enol form absorbs ($\lambda = 254$ nm) initiates both photoenolization to the *trans*-enol form and photoketonization to the diketo form (Scheme 1) [1,2].

As can be seen from the kinetic measurements, the formation of the diketo tautomeric form in PEAA during irradiation and the reverse dark reaction keto → enol are very rapid. For example, the dark reaction in acetoacetic ester (structural analogue of PEAA) takes several hours [11]. Two basic mechanisms of photoketonization are considered to explain the difference between the monomeric and polymeric β-DCCs. The first mechanism involves transformation as an internal molecular process in each β-dicarbonyl unit. This mechanism is obtained for the monomeric β-DCC [5]. Experimental evidence for the formation of the *trans*-enol form has been given by Vierov et al. [6]. In the polymeric β-DCC, the polymer chain as an alkyl substituent at the γ-position will influence the rotation around the double bond $\beta-\gamma$ in the excited state [5].
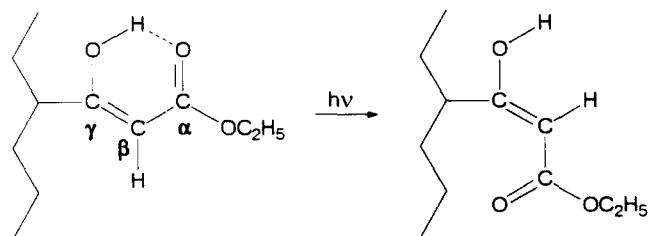
This conclusion is in accordance with previous investigations on the influence of the structure of the β-DCC on photoinduced ketonization [11].
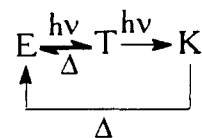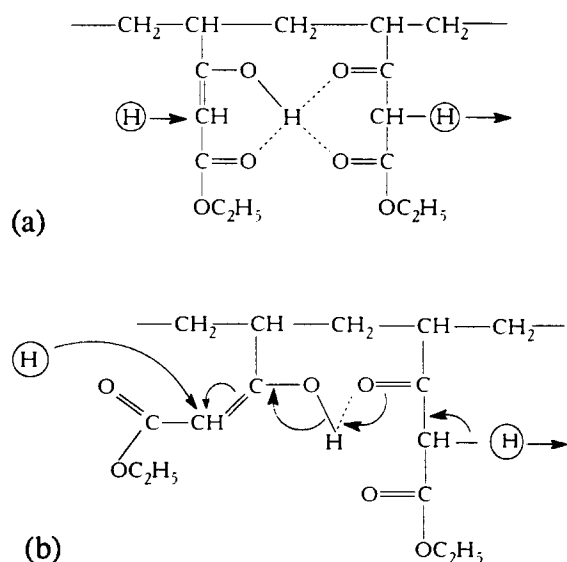

Scheme 1.

The second mechanism involves intermolecular proton transfer. There are two possibilities for the polymeric β-DCC.

(1) Transfer between two units with enol and keto tautomeric structures (Scheme 2). Such a proton transfer can be realized between two polymer chains. As shown in β-dicarbonyl esters [1], the rate of cis-enol→keto interconversion is higher than that of enolization (cis-enol→trans-enol).
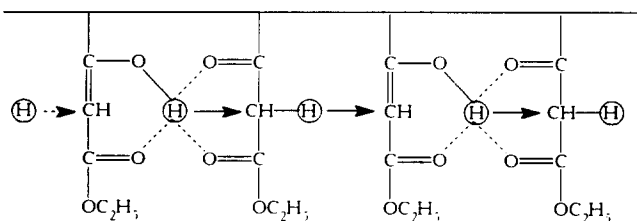
(2) Chain proton transfer (Scheme 3). The rate of this process will be very fast. Such a mechanism can explain the rapid opposite process (keto→enol).

We believe that PEAA photoketonizes via the two processes given in Schemes 2(a) and 3. The type of polymer chain is determinant. The mechanism in Scheme 2(a) will be characteristic of polymers with less orderly parts. The mechanism in Scheme 3 relies on the presence of good alternation between the enol and keto units.

It is very important to note the participation of the trans-enol form. We believe that the participation of the trans-enol form in the photoketonization of PEAA may be realized under definite conditions. The reason for this is the experiment in CH₃CN. During irradiation, the absorption maximum of cis-enol (253 nm) decreases in intensity and a new band appears at shorter wave-
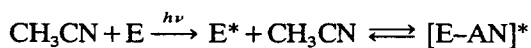
length (about 230 nm). According to Markov and Fratev [5] and Vierov et al. [6], the UV absorption maximum of the trans-enol of acetoacetic ester is 229 nm. It is important to note that, in CH₃CN, it is possible to form a "stable" exciplex with a longer lifetime between the excited enol and acetonitrile molecule [2,4]

$$CH_3CN + E \xrightarrow{h\nu} E^* + CH_3CN \rightleftharpoons [E\text{–}AN]^*$$

Such a complex cannot be formed between E (in PEAA) and the other solvents (CH_2Cl_2, $(CH_2)_2Cl_2$, $CHCl_3$). The solvating abilities of these solvents are due to the formation of hydrogen bonds [12].

The validity of Scheme 3 (fast enol–keto and keto–enol processes) is in good agreement with the existence of dimeric species in solutions of β-DCCs [13]. During the progress of our investigations, differences in the kinetics of photoinduced ketonization of freshly prepared and stable solutions of PEAA were observed (Table 2, Figs. 4 and 5). With time, the absorption band of the enol form decreased in intensity. This confirms the formation of associates between enol units, as well as between enol and keto units. Under the influence of the solvents, dissociation to individual tautomeric units takes place. The process of photoketonization can be represented by Scheme 4. However, in the polymeric β-DCC, the process of association between the different units is favoured. In stable solutions, we have

$$\text{associates} \xrightarrow{h\nu} \text{monomeric units} \xrightarrow{h\nu}$$

photoinduced ketonization
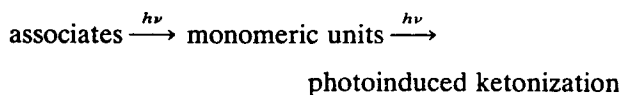
In freshly prepared solutions, we have

$$\text{monomeric units} \xrightarrow{h\nu} \text{photoinduced ketonization}$$

The presence of β-dicarbonyl units in PEAA leads to cascade proton transfer (Scheme 3). In this case, conditions are realized for good alternation between the units and the rate of photoinduced ketonization will be high. In such sandwich cage structures, the activation energy will be very low since the transfer of a proton does not involve a large change in molecular conformation. In this respect, the formation of the trans-enol form will be unfavourable. The kinetic data confirm these conclusions.

(a)

(b)

Scheme 2.

Scheme 3.

solid polymer
or stable solution   fresh solution
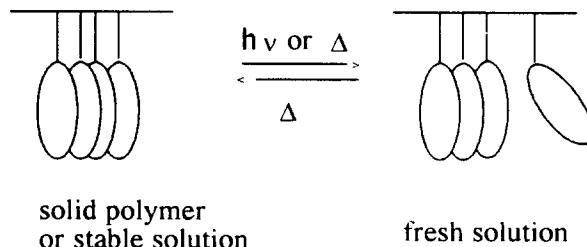
Scheme 4. Schematic representation of a sandwich complex formed between two pendant units.

References

[1] P. Markov and I. Petkov, *Tetrahedron, 33* (1977) 1013.
[2] P. Markov, I. Petkov and D. Jeglova, *J. Photochem., 8* (1978) 277.
[3] P.D. Yankov, S.M. Saltiel, I.V. Tomov, P.J. Markov and I.K. Petkov, *Laser Chem., 5* (1985) 107.
[4] P. Yankov, S. Saltiel and I. Petkov, *Chem. Phys. Lett., 128*(5, 6) (1986) 517.
[5] P. Markov and F. Fratev, *Acad. Bulg. Sci., 28* (1975) 771.
[6] D. Vierov, T. Bercovici, E. Fischer, Y. Mazur and A. Yogev, *J. Am. Chem. Soc., 99* (1977) 2723.

[7] S. Masuda, M. Tanaka and T. Ota, *Macromol. Chem., 187* (1986) 1087.
[8] C.R. Masson, V. Boekelheide and W.A. Noyes, Jr., *Technique of Organic Chemistry,* Vol. 2, Interscience, New York, 1956, p. 295.
[9] R.A. Morton, A. Hassan and T.C. Calloway, *J. Chem. Soc.,* (1934) 883.
[10] S. Masuda, M. Tanaka, R. Minato and T. Ota, *Polym. J., 18*(12) (1986) 967.
[11] I. Petkov and P. Markov, *Rev. Roum. Chem., 27*(7) (1982) 847.
[12] Th. Zeegers-Huyskens and P. Huyskens, in H. Ratajczak and W.Y. Orville-Thomas (eds.), *Molecular Interactions,* Vol. 2, MIR, Moscow, 1984, pp. 11, 116.
[13] P. Nikolov, F. Fratev, I. Petkov and P. Markov, *Chem. Phys. Lett., 83*(1) (1981) 170.