

# AM1/CI, CNDO/S and ZINDO/S computations of absorption bands and their intensities in the UV spectra of some 4(3H)-quinazolinones

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## Abstract

A detailed analysis of both frontier MOs and electronic transitions in UV spectra of 16 4-quinazolinone derivatives has been carried out in MO terms, by semiempirical methods AM1/CI, CNDO/S and ZINDO/S. On the basis of experimental and theoretical investigations by the ZINDO/S and CNDO/S methods the long-wavelength bands of 4(3H)-quinazolinone and its derivatives have been assigned to  $n \rightarrow \pi^*$  transition of the  $>C=O$  fragment and to the transition caused by intramolecular charge transfer from Ph and  $N=C-N$  fragments to  $>C=O$  group. It was shown that theoretically obtained electronic transitions applying method AM1/CI are not in agreement with experimental data observed for the 4(3H)-quinazolinone and 2,4(1H,3H)-quinazolinone. Good correlation of theoretical and experimental data has been obtained by the method ZINDO/S for the wavelengths and the molar extinction coefficients of the compounds studied. Satisfactory correlation of theoretical and experimental data has also been obtained by the method CNDO/S with singly and doubly excited configurations, for the wavelengths only. Such correlations on experimental and theoretical wavelength and molar absorption coefficients of 4-quinazolinone derivatives are carried out for the first time.

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**Keywords:** UV spectra; 4(3H)-Quinazolinones; Semiempirical calculations

## 1. Introduction

4(3H)-Quinazolinones possess wide spectrum of biological [1–6] and fungicidal activity [7,8]. Among them found CNS depressants [9], muscle relaxants [10] antimitotic anticancer [11] and inhibitors of the DNA repair enzyme poly(ADP-ribose) polymerase [5]. Furthermore, some of them can be used as a raw material to obtain other biologically active compounds [2]. Studying of the electronic structure of 4(3H)-quinazolinones by UV spectral and quantum chemical methods is important, not only for interpretation of the spectra, but also to estimate of direction of the electronic density's redistribution of the compounds, which is a determining factor of their reactivity and biological activity. Therefore, the electronic structure of 4(3H)-quinazolinones has been studied by methods UV spectroscopy, fluorescence and circular dichroism [12,13].

Furthermore, Aaron et al. [12] investigated the influence of the solvents on the positions of absorption bands in the UV-

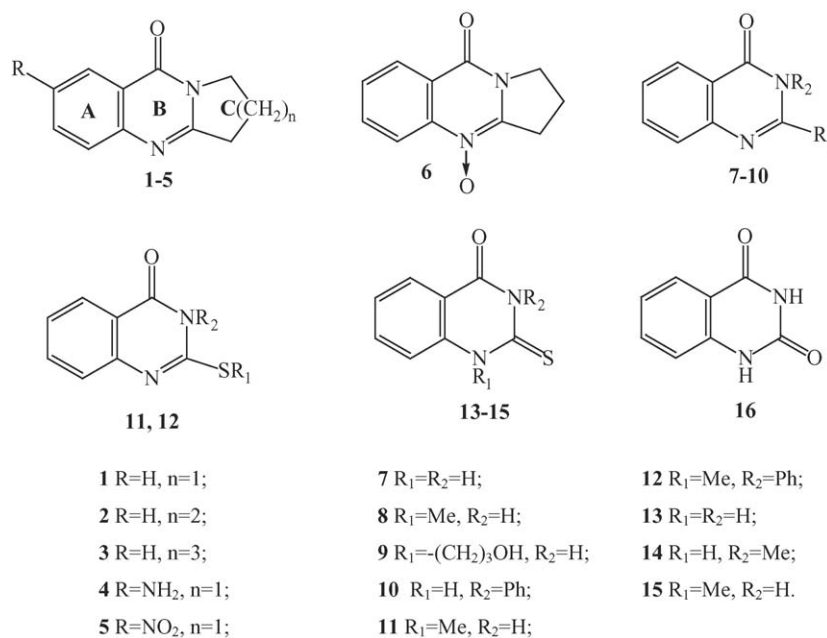
and fluorescence spectra of bicyclic 4(3H)-quinazolinones. The authors [12] using Pariser-Parr-Pople (PPP) method characterized the long wavelength bands as a  $n \rightarrow \pi^*$  transition of nitrogen atoms. However, the presence and hypsochromic shift of the maxima in acidic medium is contradict with the interpretation (Fig. 1). Therefore, a theoretical calculations have been carried out by AM1/CI [14], CNDO/S [15] and ZINDO/S [16,17] methods aiming to determine the nature of electronic transitions and correlation dependences between experimental and theoretical UV spectral characteristics of some bi- and tricyclic 4(3H)-quinazolinones (Scheme 1).

## 2. Experimental

The UV spectra were measured in ethanol solution using 1 cm quartz cells on a Perkin-Elmer Lambda 16 spectrophotometer. The concentration of compounds being in the range  $5 \times 10^{-5}$ – $5 \times 10^{-4}$  M/L. To change the pH of the solution 0.1 ml of 1 N HCl was added.

UV spectral characteristics for compounds **1–5**, **8–10** and **12** was taken from original papers [12,13,18]. The compounds **7**,

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Scheme 1.

**11**, **13–15** and **16** were synthesized by the known method [8] and have kindly been given by N.I. Mukarramov and N.P. Abdullaev. N-oxis of 2,3-trimethylene-3,4-dihydro-4-quinazolinone has been obtained by the procedure [19] and physico-chemical characteristics were identical to those described in [19].

### 3. Computational

The MO calculations have been performed using the ANCI-C (SIXW.C) program [15] and the HyperChem 6.01 software acquired from Hypercube (USA). For AM1/CI [14] and ZINDO/S [16,17] calculations of the electronic spectra (singlet transitions) configuration interaction between six occupied and unoccupied MO's (73 singly excited configurations) have been selected. Calculation by CNDO/S in the ANSI-C program [15] were performed using CI 10 eV cutoff parameter. The ground state geometry were optimized by PM3/RHF [20] method. A root-mean-square (rms) gradient in the energy of 0.005 kcal mol<sup>-1</sup> was used for the optimization criterion by Polak-Ribiere algorithm.

The two-center Coulomb integrals were calculated by using Mataga-Nishimoto expression [21]. The scaling factors  $f_{\sigma} = 1.267$  and  $f_{\pi} = 0.585$  were used to estimate two-center resonance integrals for the ZINDO/S method.

Theoretical extinction coefficients ( $\epsilon_{\text{calc.}}$ ) have been calculated by the formula (1) [15]:

$$\epsilon_{\text{calc.}} = f \times 2.699 \times \frac{10^4}{b}, \quad (1)$$

where  $b$ -line width, equal to 0.5,  $f$ -oscillator strength.

Correlation depends between experimental and theoretical positions ( $\lambda_{\text{max}}$ , nm) and intensities ( $\epsilon$ , mol<sup>-1</sup> L cm<sup>-1</sup>) of absorption bands have been obtained using LSF (Least Squares

Fit) program of FT-IR System 2000 spectrometer (Perkin-Elmer).

### 4. Results and discussion

In our previous works we have obtained using ZINDO/S method a satisfactory correlation between the positions of the bands in the experimental and theoretical spectra of the compounds **1–5** (Scheme 1) [22,23]. Therefore, in this paper we have discussed the ZINDO/S results firstly and it is compared with CNDO/S and AM1/CI results.

In experimental spectra of organic compounds some absorption bands are formed by overlapping of several transitions and a low-intensive transitions can be disappear by any intensive transitions. In this connect we have only used singlet–singlet and intensive transitions for determination of correlation dependences.

#### 4.1. Analysis of MO formations

In Figs. 1–3 the type, energy and shapes of MOs of compounds **1**, **6**, **7**, **11**, **13** and **16** are presented.

According to the obtained results by ZINDO/S method the highest occupied MO (HOMO) and second occupied MO (HOMO-1) of compounds **1**, **7** and **11** has  $\pi$ -symmetry and localized on quinazolinone fragment ( $\approx 97\%$ ) and mostly on four carbon atoms of the benzene ring ( $\approx 92\%$ ). Third occupied MO (HOMO-2) is  $n$ -type MO and localized ( $\approx 80\%$ ) on  $>C=O$  group. The interchanging the positions of last two MOs (HOMO-1 and HOMO-2) are observed on the calculation by CNDO/S method. The HOMO-1 and HOMO-2 are localized on  $>C=O$  fragment (83%) and on four carbon atoms of the benzene ring (90%), respectively.

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