

## OPTICS AND SPECTROSCOPY

### A COMPARATIVE STUDY OF THE ABSORPTION SPECTRA OF *O*-AMINOPHENOLS USING DIFFERENT QUANTUM-CHEMICAL METHODS

V. Ya. Artyukhov, O. K. Bazyl', and G. V. Mayer

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*The electron-excited states of o-aminophenol and its derivatives are calculated using the INDO method with a special spectroscopic parametrization and the method based on the density functional theory (ADF code). The results of quantum-chemical calculations are compared with the absorption spectra of the compounds under study. It is found that the INDO method used for examination of the photophysics of organic molecules provides good results on the energies and intensities of radiation electron transitions in the foregoing compounds.*

**Keywords:** *o*-aminophenol derivatives, electron absorption spectra, electron-excited states, quantum-chemical calculations.

#### INTRODUCTION

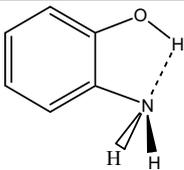
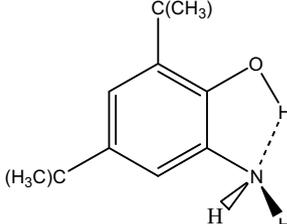
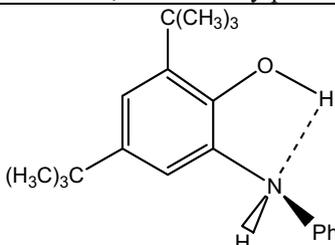
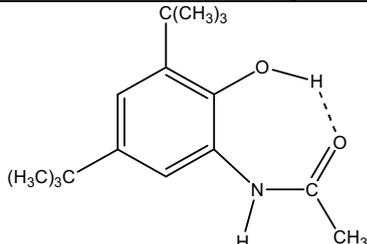
At present quantum-chemical calculations of electron states and physical-chemical properties of organic compounds are performed within various approaches: semi-empirical methods of the Hartree–Fock–Rootan theory, *ab initio* methods of the Hartree–Fock–Rootan theory, and those based on the density functional theory. The latter two methods are traditionally considered to be purely theoretical. In so doing, it is usually thought that the calculations of physical-chemical properties of organic compounds by these methods result in more reliable data and can, in principle, be performed to any accuracy. To increase accuracy, the current theoretical methods are constantly being subject to various corrections, including those semi-empirical in essence. Repeated suggestions made by M. Dewar to objectively compare the advantages and disadvantages of semi-empirical and *ab initio* methods for solving practical chemical problems have been ignored [1]. It was believed for a long time that the main disadvantage of theoretical methods, even upon development of codes based on the density functional theory, was time-consuming computations. The hopes to improve the situation are still related to the progress of computer science. It should be remembered that the same situation concerning semi-empirical methods for molecule calculation occurred in the 70s of the last century. So far, for computing, use is made of a few out of a big number of the methods. A special feature of the methods is that they are problem-oriented. They were specially developed for solving particular problems for a certain class (classes) of organic compounds. Here belong, for example, the methods developed by M. Dewar et al. On the basis of the approach, we developed a quantum-chemical code package INDO [2] with a special spectroscopic parametrization [2]. The code package was designed for solving the problems of photonics of aromatic and heteroaromatic compounds and it has been successfully applied for many years [3].

The results of quantum-chemical calculations by INDO [2] and those by the ADF package code based on the density functional [4] were compared for absorption spectra of *o*-aminophenol and its derivatives. It is well known that

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National Research Tomsk State University, Tomsk, Russia, e-mail: okbazyl@rambler.ru. Translated from *Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*, No. 12, pp. 3–7, December, 2011. Original article submitted December 15, 2010.

TABLE 1. The *o*-Aminophenol Derivatives under Study

Compound designation	Structural formula and name
AP0	 <i>o</i> -aminophenol
AP1	 2-amino-4,6-di- <i>tert</i> -butylphenol
AP2	 2-aniline-4,6-di- <i>tert</i> -butylphenol
AP3	 N-(3,5-di- <i>tert</i> -butyl-2-hydroxyphenyl)acetamide

many derivatives of aminophenols (AP) are effective antioxidants, can change the direction of free-radical processes, and exhibit antivirus activity.

The calculations were performed using a PC with a 4-core processing unit and 4 Gbytes of on-line storage.

The structural formulae of the compounds under study are given in Table 1.

## RESULTS AND DISCUSSION

It follows from the structure of the compounds and hydrogen-bond theory that an intramolecular hydrogen bond (IHB) can form between the amino and hydroxylic groups in all the molecules under study. According to the IR-spectroscopy and quantum-chemical data [5], the IHB of the O-H $\cdots$ N or N-H $\cdots$ O types can occur in *o*-aminophenols, since the OH group can be both a donor and an acceptor of protons. Due to structural features of the AP1, the IHB O-H $\cdots$ N or N-H $\cdots$ O cannot be realized simultaneously within the molecular structure of the same geometry. For each IHB type there is its own conformation of the molecule. The IHB N-H $\cdots$ O is possible in a planar molecule alone. In this case, NH<sub>2</sub>, OH, and a benzene ring are in one plane. In contrast, the IHB O-H $\cdots$ N is realized within a structure where the amino group plane is normal to that of the benzene ring. In an AP3 molecule, according to [5], only one

TABLE 2. Calculated ( $E_i$ ,  $\text{cm}^{-1} / f$ ) and Experimental ( $E_{\text{max}}$ ,  $\text{cm}^{-1} / \epsilon$ ,  $\text{M}^{-1}\cdot\text{cm}^{-1}$ ) Characteristics of Electronic  $S_0 \rightarrow S_1$ -Transitions in *o*-aminophenol

Computing method	State			
	$S_1$	$S_2$	$S_3$	$S_4$
Experiment [6]	34000 / 2950	42550 / 8320		
		AG		
INDO	36430 / 0.026	43140 / 0.118		
		DZ-basis		
INDO	36240 / 0.048	39340 / 0.079	45040 / 0.002	46570 / 0.672
ADF	37880 / 0.047	42460 / 0.0001	43770 / 0.001	47010 / 0.0001
		DZP-basis		
INDO	36200 / 0.059	39310 / 0.090		
ADF	37820 / 0.052	43770 / 0.001	45090 / 0.0003	46520 / 0.034
		TZP-basis		
INDO	36100 / 0.056	39220 / 0.086		
ADF	36990 / 0.055	39010 / 0.002	44890 / 0.0006	45100 / 0.031
		TZ2P-basis		
INDO	36140 / 0.057	39450 / 0.087		
ADF	37180 / 0.056	39180 / 0.002	44480 / 0.0005	45240 / 0.030
		QZ4P-basis		
INDO	36140 / 0.057	39250 / 0.087		
ADF	36930 / 0.054	37030 / 0.002	43920 / 0.001	44100 / 0.002

molecular structure is possible, where the molecular core should be considered planar. The IHB  $\text{O}-\text{H}\cdots\text{O}=\text{C}$  is formed in such a molecule.

At first, the AP0 molecule was calculated under varying set of basis functions. The results are summarized in Table 2. The experimental data are from [6], where hexane *o*-aminophenol solutions were examined. We would remind you that, according to the Frank-Condon principle, the energies must be compared with the maxima of the corresponding bands of the absorption spectra. The INDO method we use is not designed for optimizing the geometry of molecular ground state. Therefore, use is usually made of an averaged molecular geometry (AG) based on well-known geometric characteristics of related compounds [7]. It follows from the Table 2 data that the calculation results in this case are in reasonable agreement with experiment (concerning both energy and intensity).

The geometry of the molecular ground state was further optimized using the ADF code. In so doing, the basis set of atoms was varied with a consistent increase in the number of basis functions – DZ, DZP, TZP, TZ2P, QZ4P. In all the cases, the optimized geometry (OG) of a molecule corresponded to the IHB  $\text{O}-\text{H}\cdots\text{N}$ . Thus, the local electron pair of the nitrogen atom was switched off from conjugation with the  $\pi$ -electron system of phenyl cycle. Upon optimization of the geometry, the excited electron states were calculated using the INDO and ADF codes. All singlet states listed in Table 3 are of the  $\pi\pi^*$ -orbital nature.

Comparison of the calculated and experimental data allows the following conclusions to be drawn:

1. The INDO results for the first absorption band are virtually independent of the basis set size as to energy and increase by about a factor of two as to intensity.
2. Similar ADF results are somewhat worse in terms of energy and close in terms of intensity.
3. The INDO results for the second absorption band in terms of energy also weakly depend on the basis set size but more differ from the experimental data as compared to the case of calculations on the basis of averaged geometry. The relation between the band intensities is also dramatically decreased as compared with experiment.

TABLE 3. Calculated ( $E_i, \text{cm}^{-1} / f$ ) and Experimental ( $E_{\text{max}}, \text{cm}^{-1} / \epsilon, \text{M}^{-1} \cdot \text{cm}^{-1}$ ) Characteristics of Electron  $S_0 \rightarrow S_T$  Transitions in *o*-Aminophenol Derivatives

Calculation									Experiment [5]	
INDO (AG)			INDO (OG)			ADF (OG)			$E_{\text{max}}, \text{cm}^{-1}$	$\epsilon, \text{M}^{-1} \times \text{cm}^{-1}$
$S_i$	$E_i, \text{cm}^{-1}$	$f$	$S_i$	$E_i, \text{cm}^{-1}$	$f$	$S_i$	$E_i, \text{cm}^{-1}$	$f$		
AP1										
$S_1(\pi\pi)$	34280	0.050	$S_1(\pi\pi)$	34670	0.055	$S_1(\pi\pi)$	37180	0.061	34780	4000
$S_4(\pi\pi)$	41480	0.151	$S_4(\pi\pi)$	41470	0.175	$S_5(\pi\pi)$	45110	0.080	42900	8900
$S_9(\pi\pi)$	47150	0.660	$S_8(\pi\pi)$	47610	0.690	$S_{10}(\pi\pi)$	50750	0.207	48440	41000
$S_{10}(\pi\pi)$	47230	0.686	$S_9(\pi\pi)$	48480	0.647	$S_{11}(\pi\pi)$	51530	0.354		
AP2										
$S_1(\pi\pi)$	34360	0.060	$S_1(\pi\pi)$	35290	0.012	$S_1(\pi\pi)$	33400	0.013	34960	7500
$S_2(\pi\pi)$	35140	0.050	$S_2(\pi\pi)$	36600	0.028	$S_3(\pi\pi)$	36550	0.013	35590	7650
						$S_4(\pi\pi)$	37070	0.028		
$S_5(\pi\pi)$	40720	0.530	$S_4(\pi\pi)$	41700	0.350	$S_9(\pi\pi)$	44120	0.210	43470	19150
$S_7(\pi\pi)$	41820	0.116	$S_6(\pi\pi)$	43140	0.180	$S_{11}(\pi\pi)$	45150	0.072		
			$S_8(\pi\pi)$	45180	0.132	$S_{13}(\pi\pi)$	45800	0.044		
			$S_{10}(\pi\pi)$	46620	0.183	$S_{14}(\pi\pi)$	46280	0.56		
$S_{15}(\pi\pi)$	47380	0.832	$S_{12}(\pi\pi)$	47620	0.762	$S_{15}(\pi\pi)$	46740	0.047	49500	51000
$S_{16}(\pi\pi)$	48120	0.622	$S_{13}(\pi\pi)$	48760	0.225	$S_{19}(\pi\pi)$	50380	0.271		
AP3										
$S_1(\pi\pi)$	32520	0.093	$S_1(\pi\pi)$	33550	0.086	$S_1(\pi\pi)$	29620	0.068	34600	4000
$S_2(\pi\pi)$	37520	0.001	$S_2(\pi\pi)$	36760	0.007	$S_2(\pi\pi)$	36490	0.023		
$S_4(\pi\pi)$	38420	0.042	$S_1(\pi\pi)$	39130	0.037	$S_3(\pi\pi)$	37010	0.012		
$S_6(\pi\pi)$	41580	0.381	$S_6(\pi\pi)$	42050	0.258	$S_5(\pi\pi)$	37630	0.106	41000	5450
			$S_9(\pi\pi)$	45850	0.364	$S_9(\pi\pi)$	45180	0.074	47200	34700
$S_9(\pi\pi)$	45180	0.677	$S_{10}(\pi\pi)$	46530	0.264	$S_{12}(\pi\pi)$	45870	0.048		
$S_{11}(\pi\pi)$	47220	0.654	$S_{11}(\pi\pi)$	47310	0.587	$S_{15}(\pi\pi)$	48430	0.074		
						$S_{19}(\pi\pi)$	50000	0.081		

4. The energy of the electronic  $S_0 \rightarrow S_2$  transition calculated within the ADF code with an increase in the basis set is decreased and is in less agreement with experiment. The calculated intensities of the transition are much lower than the experimental ones.

The experimental data on the absorption spectra for AP1, AP2, AP3 in hexane are taken from [6]. These compounds were calculated using the following scheme: calculation of excited states by the INDO code using the averaged geometry; optimization of the geometry using the ADF code, and using the foregoing geometry for the INDO and ADF calculations. For the AP1 and AP2 molecules the optimized geometry corresponds to the IHB  $\text{O}-\text{H} \cdots \text{N}$ , and for the AP3 molecule – IHB  $\text{O}-\text{H} \cdots \text{O}=\text{C}$ . The calculation results are summarized in Table 3.

The experimental data cover the spectral region 33000 - 50000  $\text{cm}^{-1}$ . In different calculations, this region can correspond to 20 electronic  $S_0 \rightarrow S$  transitions. Table 3 shows those which can be used for interpretation of absorption bands (oscillator's force > 0.001). Comparison of the calculated and experimental data for AP1, AP2, AP3 results in the following conclusions:

1. The INDO results for the averaged and optimized geometries of all the compounds reproduce the absorption spectra very well in terms of band energy and quite satisfactorily in terms of intensity.

2. The ADF results for the optimized geometries of AP1, AP2 reproduce the absorption spectrum with a short-wavelength shift and show low band intensities.

3. For an AP3 molecule the ADF results are, in contrast, shifted to the long wavelength range in terms of energy and are in disagreement in terms of intensity in the 45000–50000 cm<sup>-1</sup> range.

Thus, our calculations of electron-excited states of the *o*-aminophenol derivatives by the semiempirical INDO method with a special spectroscopic parametrization and by the method based on the density functional theory (ADF code) and comparison of the calculated and experimental data show that the INDO method we use for investigation into the photophysics of organic compounds gives fairly good results in terms of energies and intensities of radiative electron transitions in the compounds under study.

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