Quantum-chemical study of spectral-luminescent and physical-chemical properties of toluidines

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The quantum-chemical study of spectral and photophysical properties of *o*-, *m*- and *p*-toluidines by the PNDO method with spectroscopic parameterization has been carried out. The rate constants of photophysical processes have been calculated. The features in the effect of the position of methyl group in the phenyl radical and electronic excitation on the proton-donating and proton-accepting properties of substituted aniline have been revealed.

Introduction

To systematically study how the position and the kind of a substituent in the phenyl radical of aniline affect the spectral properties, as well as proton-donating and proton-accepting of primary amines is an urgent problem, since amines are widely used in industry and medicine.

Earlier[1] the methods of electronic spectroscopy and quantum chemistry have been used to study how the position of the methoxygroup in the phenyl radical of aniline affects the spectral, geometric, and photophysical characteristics of anisidines. It has been shown that the change of the methoxygroup position in the series of molecules: ortho-, meta-, and para-anisidine, leads to significant variations of the rate constants of radiative and nonradiative processes. The presence of the intermolecular NH...O bond in orthoaniside leads to nonequivalent population of the N–H bonds in amino group, and this affects the proton-donating properties of the hydrogen atoms in these bonds. It has been shown that the electronic excitation decreases the proton-accepting properties of the nitrogen atoms in amino group and oxygen in the methoxygroup.

It seems interesting to study how the position of the methyl group in the phenyl ring affects the spectral-luminescent and physical-chemical properties of toluidines.

Technique of investigation

The absorption spectra of ortho-, meta-, and para-toluidines were recorded with a Shimadzu UV-1601 spectrophotometer.

Isooctane was taken as a solvent. The concentration of toluidines in solutions was about $4 \cdot 10^{-4}$ mol/liter.

For understanding the nature of absorption in the spectral range from 30 000 to 46 000 cm^{-1}, the quantum-chemical calculations were invoked. The energy levels of the electronically excited states of the molecules studied were calculated by the PNDO (partial neglect of differential overlapping) method with spectroscopic parameterization.[2] The rate constants of the intramolecular photophysical processes (internal and singlet-triplet conversion) were estimated according to Ref. 3.

The proton-accepting properties of functional groups of toluidines were determined using the MEP (molecular electrostatic potential) method.[3]

The geometry of ortho-, meta-, and paratoluidines was taken according to Refs. 4 and 5. The plane XY coincided with the molecular plane, and the axis X of the Cartesian coordinate system was taken coincident with the long molecular axis.

Discussion

As can be seen from the absorption spectra of orthotoluidine, metatoluidine, and paratoluidine molecules in the region under study (Fig. 1), these molecules are characterized by the presence of two broad absorption bands peaking at 34 800 and 42 500 cm^{-1}.

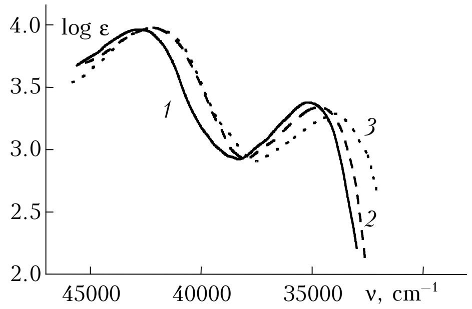

Fig. 1. Absorption spectra of toluidines in isooctane: orthotoluidine (0.37 mmol/liter) (*1*), metatoluidine (0.41 mmol/liter) (*2*), paratoluidine (0.36 mmol/liter) (*3*).

The quantum-chemical calculations indicate that the profile of the absorption band in the long-wave region is formed by the transition $S_0 \rightarrow S_1(\pi\pi^*)$ (Table 1). According to the calculations, the absorption band in the middle part of the spectrum (42000–47000 cm^{-1}) is formed by two electronic transitions of $\pi\pi^*$- and $\pi\sigma^*$-types for all the toluidines. The intensity of this absorption band is largely due to the transitions $S_0 \rightarrow S_3(\pi\pi^*)$ in ortho- and paratoluidine

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and $S_0 \to S_2(\pi\pi^*)$ in metatoluidine (Table 1). Note that in anisidines the spectral manifestations in the absorption bands in the long-wave and middle spectral ranges[1] are similar to those in methylanilines considered in this paper.

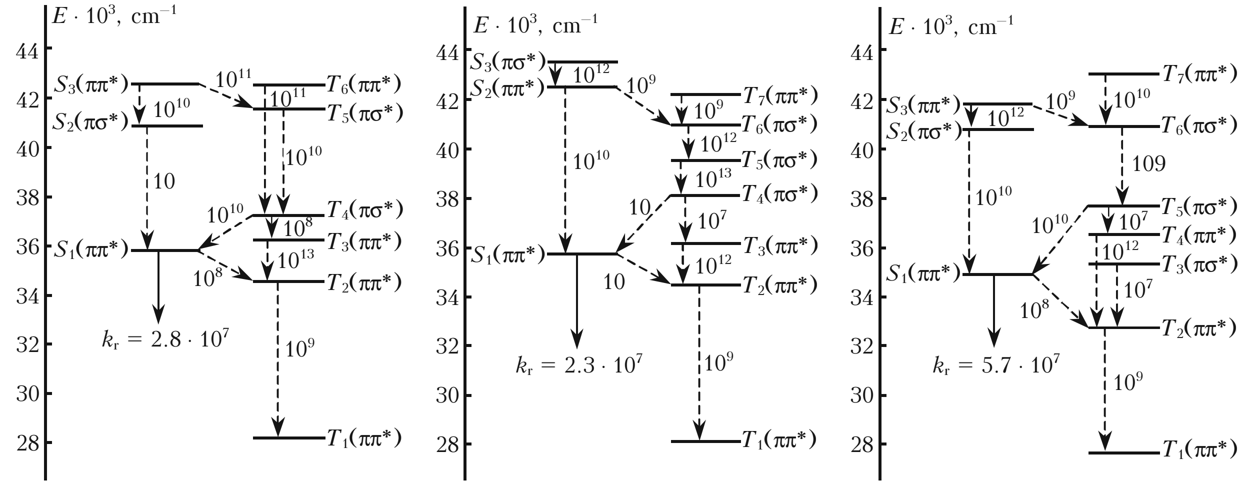
Table 1 summarizes the values of dipole moments of molecules in different excited electronic states. Note that for the ground state a good agreement was obtained between the calculated dipole moments and the experimental data.[6] The calculated values of the dipole moments for ortho-, meta-, and paratoluidines in the ground state were found to be 2.21, 1.97, and 1.82 D, while the experimental ones are 1.61, 1.49, and 1.36 D, respectively. From Table 1 it follows that the electronic excitation leads to an increase in the dipole moment of toluidines.

Figure 2 shows the scheme of energy levels and the rate constants of intramolecular photophysical processes in ortho-, meta-, and paratoluidine. It follows from Fig. 2 that the change in the position of the methyl group in the studied molecules results in variation of the rate constants of radiative and nonradiative processes. Thus, for example, the substitution of hydrogen in the para-position of the phenyl ring of aniline in the methyl group results in that the radiative constant k_r almost doubles as compared to that of the ortho- and meta-substitutions.

Table 1. Characteristics of electronic transitions for free toluidine molecules

Compound	State	Experiment		Calculation			
		E_i, cm^{-1}	f	E_i, cm^{-1}	f	P	μ, D
Orthotoluidine	$S_1(\pi\pi^*)$	35130	0.035	35870	0.031	Y, Z	3.29
	$S_2(\pi\sigma^*)$			40730	0.004	X, Z	3.01
	$S_3(\pi\pi^*)$	42860	0.148	42390	0.144	X	3.99
Metatoluidine	$S_1(\pi\pi^*)$	34790	0.032	35780	0.025	Y	2.66
	$S_2(\pi\pi^*)$	42300	0.161	42370	0.172	X	2.77
	$S_3(\pi\sigma^*)$			43190	0.003	X	5.04
Paratoluidine	$S_1(\pi\pi^*)$	34170	0.032	34930	0.065	Y	2.39
	$S_2(\pi\sigma^*)$			41050	0.026	X	5.47
	$S_3(\pi\pi^*)$	42190	0.172	41340	0.257	X	3.13

Note. E_i is energy; f is oscillator strength; P is polarization of an electronic transition; μ is molecular dipole moment in excited states.



a *b* *c*

Fig. 2. Scheme of excited electronic states of orthotoluidine (*a*), metatoluidine (*b*), and paratoluidine (*c*). Dashed arrows indicate the most efficient photophysical processes, and numbers are the rate constants of these processes, in s^{-1}.

Table 2. MEP values (kJ/mol) for toluidines in different electronic states

Molecule	Molecular fragments	State			
		S_0	$S_1(\pi\pi^*)$	$S_2(\pi\pi^*)$ or $S_3(\pi\pi^*)$	$T_1(\pi\pi^*)$
Orthotoluidine	amino group	–365	–196	–184	–232
	phenyl	–50	–98	–102	–89
Metatoluidine	amino group	–359	–201	–207	–244
	phenyl	–53	–97	–81	–85
Paratoluidine	amino group	–366	–189	–195	–248
	phenyl	–44	–95	–84	–71

Note. The state $S_2(\pi\pi^*)$ is for metatoluidine and $S_3(\pi\pi^*)$ is for ortho- and paratoluidines.

Analysis of the results of the quantum-chemical calculations for metatoluidine (Fig. 2) suggests that the quantum yield of fluorescence for this molecule must be independent of the energy of excitation quantum up to 42000 cm^{-1}. This is connected with the fact that the excitation of $S_0 \rightarrow S_2(\pi\pi^*)$ in metatoluidine by the channels of singlet–triplet conversion populates the state $T_4(\pi\sigma^*)$. The state T_4 more efficiently depopulates by the channel of triplet–singlet conversion $T_4(\pi\sigma^*) \rightarrow S_1(\pi\pi^*)$ than by the channel of internal conversion $T_4(\pi\sigma^*) \rightarrow T_3(\pi\pi^*)$.

It follows from Fig. 2 that the main nonradiative channel for deactivation of the fluorescent state is singlet–triplet conversion $S_1(\pi\pi^*) \rightarrow T_2(\pi\pi^*)$.

Table 2 summarizes the MEP values as calculated for different excited electronic states of toluidines. It can be seen from Table 2 that at electronic excitation the proton-acceptor properties of the phenyl ring increase and those of the nitrogen atom of amino group decrease.

Thus, electronic excitation leads to significant redistribution of the proton-accepting capability of phenyl and nitrogen atom of amino group. This fact should be necessarily taken into account when considering the process of complexing the intermolecular hydrogen bond, in which methylanilines play the role of proton-acceptors.

Acknowledgments

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