DOI 10.1007/s11182-021-02469-1
Russian Physics Journal, Vol. 64, No. 8, December, 2021 (Russian Original No. 8, August, 2021)

OPTICS AND SPECTROSCOPY

SPECTRAL-LUMINESCENT PROPERTIES AND PHOTOLYSIS OF SOME PHENOL DERIVATIVES

O. N. Tchaikovskaya, O. K. Bazyl, and E. N. Bocharnikova UDC 539.194:535.37

The spectral-luminescent properties and photolysis of phenol and some of its derivatives have been considered experimentally and by methods of quantum chemistry. It has been shown that the substitution with a methyl group (p-cresol) and the introduction of the second benzene ring (bisphenol A) lead to a shift of absorption bands toward longer wavelengths and some changes in their intensity. The non-planar structure of p-cresol and bisphenol A promotes an increase in the efficiency of singlet-triplet conversion and a decrease in the fluorescence quantum yield. Results of calculations have established the mechanisms of photolysis of the considered molecular systems. It has been shown that the O–H bond in phenol and p-cresol is broken by the pre-dissociation mechanism. Photolysis of bisphenol A upon exposure to solar radiation proceeds by the mechanism of direct dissociation, but with a noticeable potential barrier (~12000 cm^{-1}).

Keywords: phenol, *p*-cresol, bisphenol A, photophysical processes, quantum-chemical calculation, photolysis, spectral-luminescent properties.

INTRODUCTION

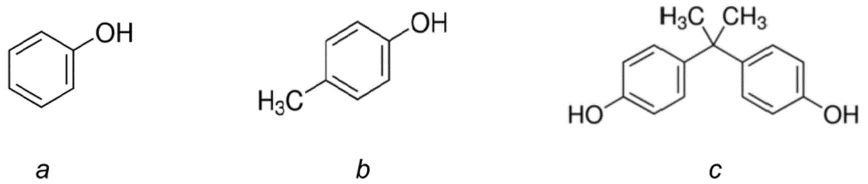
The wide circulation of phenols in the environment is caused by their physical and chemical properties, namely, their good solubility both in the water environment and organic matrices, low vapor pressure, and high reactivity [1–3]. Phenols form the group of aromatic organic compounds that contain hydroxyl groups attached to benzene rings. The phenol compounds are inhibitors of free radical processes and are widespread in biomedicine [4–6]. Natural phenols are used as antioxidants. Phenol derivatives find application in therapy of chronic inflammatory immune diseases such as hepatitis, dermatitis, rheumatism, and eczema. They are used to treat wounds and to protect tissues against penetrating radiation and action of strong oxidizers [7]. Phenol and *p*-cresol are well-known antibacterial agents with wide spectrum of action, have anti-inflammatory properties, and act on gram-positive and gram-negative flora and fungal microorganisms; therefore, they are actively used as antibacterial additives to polymers [8, 9]. The study of phenols by optical and quantum-chemical methods is urgent in connection with high pharmacological activity of these compounds [10–13].

Phenol and its main derivatives are referred to main toxicants polluting the environment. They belong to the compounds of the first and third classes of danger. Moreover, *p*-cresol and bisphenol are included in many composite polymeric materials as monomers and antioxidating or preserving additives. For example, bisphenol A is one of the key monomers used in manufacture of epoxy resins and polycarbonate plastics [14, 15] and as a hardener and stabilizer in polymeric materials. Phenols enter surface waters with drains of oil refining, oil shale processing, wood chemical treatment, by-product coke, and aniline paint industrial enterprises. In waters they can be found in dissolved forms as

---

National Research Tomsk State University, Tomsk, Russia, e-mail: tchon@phys.tsu.ru; olga.k.bazyl@gmail.com; bocharnikova.2010@mail.ru. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 8, pp. 3–8, August, 2021. Original article submitted April 7, 2021.

1064-8887/21/6408-1385 ©2021 Springer Science+Business Media, LLC



a *b* *c*

Fig. 1. Structural formulas of the considered compounds: phenol (*a*), *p*-cresol (*b*), and bisphenol A (*c*).

phenolates and free phenols. When treating water containing phenol impurity with chlorine, very dangerous organic toxicants – dioxins – can be formed. The phenol content in polluted natural waters can reach several hundreds micrograms per liter. The discharge of phenolic waters into water reservoirs and water streams sharply deteriorates their general sanitary state, thereby influencing living organisms not only due to toxicity, but also due to significant change of biogenic elements and dissolved gases (oxygen and carbon dioxide). The process of self-purification of water reservoirs from phenol proceeds rather slowly, and its traces can be carried away by water flows at large distances. The presence of even a very small amount of phenol in water intended for the economic and drinking purposes considerably deteriorates its quality.

In the present work, results of experimental and theoretical investigation of spectral-luminescent properties of three phenol molecules: phenol (C_6H_5OH), *p*-cresol ($CH_3C_6H_4OH$), and bisphenol A (BPA, $(CH_3)_2C(C_6H_4OH)_2$) are presented. Experimental absorption, fluorescence, and fluorescence excitation spectra of these compounds in hexane are obtained. Quantum-chemical calculations of electronic structures and spectral characteristics of the considered molecules are carried out.

OBJECTS AND METHODS OF RESEARCH

The objects of research were 99.8 % pure phenol (C_6H_5OH), *p*-cresol ($CH_3C_6H_4OH$), and bisphenol A (BPA, $(CH_3)_2C(C_6H_4OH)_2$) from Sigma Aldrich. Structural formulas of the considered compounds are shown in Fig. 1.

As a solvent, 99.9 % pure ethyl alcohol C_2H_5OH from Sigma Aldrich was used. The experiment was performed at a temperature of 20°C. The spectral-luminescent characteristics of the solutions were recorded with an SM 2203 spectrofluorimeter (SOLAR, Belarus) [16]. Quantum-chemical calculations were performed using the software package based on the semiempirical method of intermediate neglect of differential overlap with original spectroscopic parameterization (INDO/S) [17]. The quantum-chemical programs and techniques used to estimate the rate constants of photoprocesses used to solve spectroscopy problems have been developed by professor G. V. Mayer and professor V. Ya. Artyukhov. The ground state was optimized using the Austin Model 1 (AM1) method (or the Austin model No. 1) [18].

RESULTS AND DISCUSSION

Spectral characteristics of considered molecules in nonpolar solvents

A comparative analysis of the absorption and fluorescence spectra of phenol derivatives in nonpolar solvent (hexane) showed that phenol has characteristic absorption in the UV range of the spectrum. Two absorption bands of phenol with maxima approximately at 37000 and 47400 cm^{-1} were clearly pronounced in the electronic absorption spectrum, and both bands had vibrational structures. The structure of the long-wavelength band vanished when going from nonpolar to polar solvent or incorporation of the CH_3 group (*p*-cresol). Calculations showed that the long-wavelength absorption band of phenol in hexane is formed by the single $\pi\pi^*$-type $S_0 \to S_1$ electronic transition. This circumstance indirectly testifies to the vibrational structure of the long-wavelength phenol band. According to the

TABLE 1. Experimental and Theoretical Location of the Absorption Bands in Spectra of Phenol, *p*-Cresol, and BPA in Hexane

Calculation			Experiment
State	E_i, cm^{-1}	f	$E_{\max}$, cm^{-1}
Phenol			
$S_1(\pi\pi^*)$	37200	0.028	37800
$S_2(\pi\pi^*)$	39900	0.031	
$S_6(\pi\pi^*)$	48100	0.635	47400
$S_8(\pi\pi^*)$	51000	0.832	~52910
$T_1(\pi\pi^*)$	27000	–	28600 [20]
n-Cresol			
$S_1(\pi\pi^*)$	36000	0.101	36100
$S_6(\pi\pi^*)$	47700	0.594	45500
$T_1(\pi\pi^*)$	24600	–	–
Bisphenol A			
$S_1(\pi\pi^*)$	35100	0.063	36400
$S_2(\pi\pi^*)$	35600	0.053	
$S_3(\pi\pi^*)$	36100	0.121	
$S_5(\pi\pi^*)$	38500	0.402	41700
$S_6(\pi\pi^*)$	40300	0.293	
$T_1(\pi\pi^*)$	24000	–	–

TABLE 2. Calculated Rate Constants of Photophysical Processes and Quantum Yields of Phenol and Some of Its Derivatives

Molecule	k_{ic}, s^{-1}	k_{r}, s^{-1}	k_{ST}, c^{-1}	ϕ_{theor}	$\phi_{\exp}$*
Phenol	$2\cdot10^2$	$3\cdot10^7$	10^8	0.23 [26, 27]	0.2
p-Cresol	10^3	$9\cdot10^7$	$2\cdot10^{10}$	0.005	0.01
Bisphenol A	$5\cdot10^3$	$6\cdot10^7$	$2\cdot10^{10}$	0.003 [28]	0.001

Note. *Experimental values are given for hexane.

experimental results, the maxima of the vibrational bands of phenol and *p*-cresol in hexane are centered at ~33000 cm^{-1}. In the absorption spectrum of BPA in hexane, the maximum of the absorption band was at 36500 cm^{-1}, and the maximum of the fluorescence band was at 33560 cm^{-1}.

The optimized geometries of *p*-cresol and BPA (bond lengths, valences, and torsion angles) indicate their nonplanar character. The exact structural parameters of the considered molecules (bond lengths, valences, and torsion angles) are unknown; therefore, the geometry of the ground state is optimized by the method of molecular mechanics (program MM2 Chem Office) [19]. A consequence of the nonplanar structure of *p*-cresol and BPA is the mixed character of the orbital nature of excited states. Therefore, the reference of the excited state to an orbital type testifies only to its primary contribution. The energy values obtained by quantum-chemical calculations of isolated considered molecules are presented in Table 1. The experimentally observed maxima of the absorption bands of examined compounds are in good agreement with the calculated data.

According to the results of quantum-chemical calculations [21], the absorption of phenol and *p*-cresol in the region of 35000–36000 cm^{-1} is caused by single $\pi\pi^*$-type $S_0 \rightarrow S_1$ electronic transition; therefore, the observed structurization of the electronic band displays its vibrational structure. The results of quantum-chemical calculations of isolated phenol molecules showed that the σ-type molecular orbitals localized on the OH bond (Table 2) do not take part in formation of the wave functions of excited states up to 50000 cm^{-1}. Incorporation of the CH_3 group into the

TABLE 3. Population of the O–H Bond in the Ground and Indicated Excited States

Compound	States						
	S_0	$S_1(\pi\pi^*)$	$S_2(S_3)(\pi\pi^*)$	$S_2(\pi\sigma^*)$	S_D	$T_4(\pi\sigma^*)$	T_D
Phenol	0.578	0.578	0.578	–	–0.176	0.570	–0.066
p-cresol	0.578	0.578	0.578	0.578	0.109	0.557	–0.130

benzene ring leads to the decrease of the calculated energy of electronic transitions, the bathochromic shift of the band maxima in the long-wavelength and middle regions of the spectrum, and the increase of the long-wavelength absorption band intensities. The location of vibronic levels in the electronic absorption bands of *p*-cresol is manifested in the form of two inflections in regions of 36000 and 46000 cm^{-1}. As to the electronic transitions of phenol and *p*-cresol in the region of the spectrum at ~50000 cm^{-1}, they are localized only on carbon atoms of the aromatic ring of molecules.

To understand ways of transformation of the electronic excitation energy in the considered compounds, the rate constants of photophysical processes were calculated, including radiative (k_r) and nonradiative (internal (k_{ic}) and singlet-triplet (k_{ST})) conversions. An analysis of rate constants of photophysical processes allowed us to estimate the most probable ways of excitation energy transformation [22–25] and the quantum fluorescence yield. The rate constants of the considered molecules are given in Table 2.

The energy level diagrams of electronically excited levels of the considered molecules [29] demonstrated that when going from phenol to bisphenol, the *ST* conversion efficiency increased in the series: phenol – *p*-cresol – bisphenol A.

A comparison of quantum yields for the considered molecules of the phenol class showed that the presence of methyl groups in the *p*-cresol structure opens the effective channel of intercombination conversion resulting in a nearly twofold decrease of the quantum fluorescence yield compared to that of the initial phenol (Table 2).

Photolysis of the considered molecules

It is well known that the O–H bond in phenol and *p*-cresol molecules is broken upon exposure to radiation [30, 31]. To assign experimental results on photo-induced degradation of molecules, quantum-chemical calculations of phenol, *p*-cresol, and BPA photolysis were performed and the mechanism of photoreaction and the efficiency of O–H bond braking were considered depending on the molecular interaction and the excitation energy.

The probability of chemical bond breaking is determined by the degree of localization of the excitation energy absorbed by the molecule on the broken bond and the decrease of the bond strength upon excitation to the electronic state in comparison with the ground state of the molecule; moreover, the energy of the excited state should be higher than the bond dissociation energy. No less important is the possibility of effective population of the photodissociation level, the direct excitation of the state, or the intramolecular relaxation of the electronic excitation energy.

The reactions of C–O bond breaking are not characteristic for phenols, because the oxygen atom is strongly attached to the carbon atom of the benzene ring due to participation of its unshared electron pair in the conjugated system. The mutual influence of atoms in the phenol molecule is manifested not only as special features in the hydroxyl group behavior, but also as a higher reactivity of the benzene nucleus. The hydroxyl group increases the electronic density on the benzene ring, especially, in *orto*- and *para*-positions.

Calculations of the population of O–O bonds in isolated phenol and *p*-cresol molecules showed that the population (strength) of the bond in all $\pi\pi^*$- and $\pi\sigma^*$-type states formed without participation of the O–H group remained practically unchanged upon electronic excitation. The bond strength of the $\pi\sigma^*$-type singlet and triplet states the σ *-orbitals of which are localized on the O–H bond considerably decreased (Table 3).

The potential curves of all electronically excited phenol and *p*-cresol states in the region up to 50000 cm^{-1} correspond to the stable molecule, and those of the S_D and T_D states correspond to the decay curves when choosing the O–O bond length as the coordinate reaction (here $S_D \equiv S(\pi\sigma^*)_{OH}$ and $T_D \equiv T(\pi\sigma^*)_{OH}$). Situations for phenol and *p*-cresol are identical [32]. The potential curves of all photodissociation states with energy below ~50000 cm^{-1} and the employed excitation states (n = 43670 and 45450 cm^{-1} [33]) are linking in character. The O–H bond strength changes weakly upon excitation, and the MOs localized on this bond do not take part in the formation of the σ*-state. This allows us to conclude that the photo-induced breaking of the bond occurs by the straightforward dissociation mechanism, and the most probable mechanism is pre-dissociation.

The photolysis of phenol and *p*-cresol considered above showed that photo-induced breaking of the O–H bond occurs under excitation. The situation differs for BPA. Since we consider the process of molecule degradation upon exposure only to solar radiation whose short-wavelength boundary on the Earth surface is at ~290 nm (~34480 cm^{-1}), the energy of the photodissociative state localized on the O–H bond considerably exceeds this value. Analogous situation is also characteristic for single $C–CH_3$ bonds. As to the energy of states localized on single $C_5–C_8$ or $C_8–C_{11}$ bonds of BPA, it is much closer to ~34480 cm^{-1}.

In quantum-chemical calculations, the electronic density is distributed among atoms in the molecule and their bonds. The value of the electron density on the chemical bond corresponds to its strength; hence, its increase testifies to bond strengthening (energy increase), and its decrease corresponds to bond weakening. From the results of BPA calculations [34] it follows that the maximum decrease of the considered bond strengths is characteristic for $C_{8–11}$ and $C_{5–11}$ bonds in singlet and triplet states localized on these bonds. In the S_0 state the population of the $C_8–C_{11}$ bond was $P_{8–11} = 0.783e$, and in the $S_3(\pi\sigma_{8–11})$ state, it decreased to $0.216e$. Moreover, the population (strength) decrease of these bonds in the assumed photodissociative states is characteristic both for singlet and triplet states of this type.

Having established the form of the potential curve for several $S_1(\pi\pi^*)$, $S_3(\pi\sigma_{8–11}^*)$, and $T_5(\pi\sigma_{8–11}^*)$ states of BPA, we have chosen the length of the $C_8–C_{11}$ as the reaction coordinate for quantum-chemical calculations of these states with varying bond length of one of the single bonds. For the $S_1(\pi\pi^*)$ state, the linking curve was characteristic, whereas for the singlet and triplet $\pi\sigma_{8–11}^*$-type states, the repulsion curves with a noticeable potential barrier were characteristic.The single $C_8–C_{11}$ bond can break, but with a potential barrier; this makes the photolysis of the molecule upon exposure to sunlight ineffective. The energy of the $S_3(\pi\sigma_{8–11}^*)$ state makes its direct population possible, and the photodissociative triplet state is populated by the $S_1(\pi\pi^*) \rightarrow T_6(\pi\sigma_{5–8–11})$ conversion.

CONCLUSIONS

Based on the results of our research, we can conclude the following.

1. The absorption spectra of the substituted molecules are shifted toward longer wavelengths compared tophenol. The energies of the BPA, *p*-cresol, and phenol fluorescence bands differ slightly. Significant differences in quantum fluorescence yields of the considered compounds are caused by different geometries of the substituted molecules compared to the phenol geometry. The non-planar *p*-cresol and BPA geometry caused the singlet-triplet conversion in these molecules to be intensified compared to flat phenol and, as a consequence, to the reduced quantum fluorescence yield.
2. During photolysis of phenol and *p*-cresol, O–O bond breaks by the pre-dissociation mechanism, whereas the BPA photolysis is accompanied by breaking of the bond between the intermediate and phenolic fragments of the molecule by the straightforward dissociation mechanism.
3. The presence of methyl groups in substituted phenol changes to a lesser degree the absorption and fluorescence spectra, but noticeably changes the singlet-triplet conversion efficiency and the photolysis mechanism.

These results were obtained within the framework of the State Assignment of the Ministry of Education and Science of the Russian Federation (Project No. 0721-2020-0033).

REFERENCES

1. L. N. Aleksandrova, Organic Substance of Soil and Processes of Its Transformation [in Russian], Nauka, Leningrad (1980).
2. N. N. Alykov, E. V. Iglina, E. S. Savelyeva, *et al.*, Ecol. Syst. Dev., N. 9, 38–40 (2008).
3. L. I. Kozubova, Organic Pollutants of Drinking Water: An analytical Review [in Russian], State Public Scientific Technical Library of the Siberian Branch of the Russian Academy of Sciences, Novosibirsk (1993).

4. V. V. Ershov, G. A. Nikiforov, and A. A. Volod'kin, Sterically Hindered Phenols, Khimiya, Moscow (1972).
5. V. A. Roginskii, Phenol Antioxidants: Reactivity and Efficiency, Nauka, Moscow (1988).
6. B. Halliwell and J. M. C. Gutteridge, Free Radicals in Biology and Medicine, Clarendon Press, Oxford (1999).
7. O. I. Shadyro, V. L. Sorokin, G. A. Ksendzova, *et al*., Bioorg. Med. Chem. Lett., **18**, No. 7, 2420–2423 (2008).
8. J. L. Coughlin, B. Winnick, and B. Buckley, Anal. Bioanal. Chem., **401**, No. 3, 995–1002 (2011).
9. F. Vela-Soria, O. Ballesteros, A. Zafra-Gómez, *et al*., Anal. Bioanal. Chem., **406**, No. 15, 3773–3785 (2014).
10. M. V. Bel'kov, G. A. Ksendzova, G. I. Polozov, *et al*., Zh. Prikl. Spektrosk., **75**, No. 1, 69–74 (2008).
11. G. A. Ksendzova, G.L. Polozov, I. V. Skornyakov, *et al*., Opt. Spektrosk., **102**, No. 4, 602–607 (2007).
12. M. V. Bel'kov, G. A. Ksendzova, P. V. Kuzovkov, *et al*., Zh. Prikl. Spektrosk., **74**, No. 5, 635–641 (2007).
13. O. K. Bazyl', V. Ya. Artyukhov, G. V. Maier, *et al*., Opt. Spektrosk., **107**, No. 4, 596–606 (2009).
14. D. Zhou, F. Wu, N. Deng, *et al*., Water Res., **38**, No. 19, 4107–4116 (2004).
15. Yu.-P. Chin, P. L. Miller, L. Zeng, *et al*., Environ. Sci. Technol., **38**, No. 22, 5888–5894 (2004).
16. GOST 12997-84 "GSP Products. General Specifications," TU BY 100424659.013-2006 "Spectrofluorimeter SM 2203."
17. V. Ya. Artyuhov and A. I. Galeeva, Russ. Phys. J., **29**, No. 11, 949–952 (1986).
18. G. V. Mayer, V. Ya. Artyukhov, and A. V. Karypov, Opt. Spektrosk., **66**, No. 4, 823–826 (1989).
19. A. I. Kitaigorodskii, P. M. Zorkii, and V. K. Belskii, Structure of an Organic Substance (Data of Structural Research, 1929–1970) [in Russian], Nauka, Moscow (1980).
20. D. S. McClure, J. Chem. Phys., **17**, 905 (1949).
21. Yu. P. Morozova, O. N. Tchaikovskaya, and N. Yu. Vasil'eva, Zh. Fiz. Khim., **72**, No. 2, 272–279 (1998).
22. R. Zagradnik and R. Polak, Fundamentals of Quantum Chemistry [Russian translation], Mir, Moscow (1979).
23. V. Ya. Artyukhov and O. K. Bazyl', Computer Quantum Chemistry: Educational-Methodical Manual, Publishing House of Tomsk State University, Tomsk (2010).
24. V. A. Blatov, A. P. Shevchenko, L. G. Samsonova, *et al*., Semiempirical Computational Methods of Quantum Chemistry: A Textbook, "Univer Grupp" Publishing House, Samara (2005).
25. V. A. Bakulev, Yu. Yu. Morzherin, and Yu. O. Subbotina, Quantum-Chemical Calculations of Organic Molecules [Electronic Resource], Ural Federal University Publishing House, Ekaterinburg (2004).
26. C. A. Parker, Photoluminescence of Solutions [Russian translation], Mir, Moscow (1972).
27. S. Udenfriend, Fluorescence Assay in Biology and Medicine [Russian translation], Mir, Moscow (1965).
28. É. M. Sokolov, L. É. Sheinkman, and D. V. Dergunov, Water Chem. Ecol., No. 4, 26–32 (2012).
29. E. N. Bocharnikova, O. N. Tchaikovskaya, and V. Ya. Artukhov, Russ. Phys. J., **62**, No. 9, 1700–1707 (2020).
30. G. B. Tolstorozhev, M. V. Bel'kov, T. F. Raichenok, *et al*., Opt. Spektrosk., **115**, No. 5, 807–816 (2013).
31. V. A. Svetlichnyi, O. N. Tchaikovskaya, O. K. Bazyl', *et al*., High Energy Chem., **35**, No. 4, 258–264 (2001).
32. O. N. Tchaikovskaya, Spectral-luminescent properties, photophysical, and photochemical processes in hydroxyaromatic compounds excited by ultraviolet radiation, Doctoral Thesis in Physical and Mathematical Sciences, Tomsk (2007).
33. M. G. Kang, H.-E. Han, and K.-J. Kim, J. Photochem. Photobiol. A, **125**, 119–125 (1999).
34. E. N. Bocharnikova, O. N. Tchaikovskaya, O. K. Bazyl', *et al*., Adv. Quantum Chem., **81**, 191–217 (2020).