Chemistry of Natural Compounds, Vol. 41, No. 5, 2005

TAUTOMERISM OF THE NATURAL ANTHRAQUINONES PHYSCION AND EMODIN AND THEIR ANALOGS

V. Ya. Fain, B. E. Zaitsev, and M. A. Ryabov

UDC 547.673.6:544.183.26:544.127:535.34

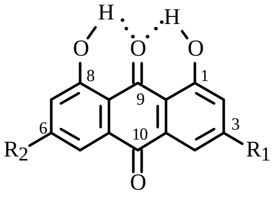
The 9,10-1,10-anthraquinoid tautomer was found to be characteristic of physcion and emodin and their analogs in solutions using spectrophotometric, quantum-chemical, and correlation methods. Ionization of these compounds was accompanied by a shift in tautomeric equilibrium. In alkaline solutions 1,10-anthraquinoid anions with a single α-hydroxy that were stabilized by an intramolecular H-bond were formed. Tautomerism occurred in both the ground and excited states of the molecules.

Key words: natural anthraquinones, physcion, emodin, citreorosein, chrysazin, chrysophanol, electronic absorption spectra, quantum-chemical calculation, correlation analysis, tautomerism, ionization.

In a previous report [1] it was demonstrated that the chemistry of natural anthraquinones [2, 3] can no longer be considered exclusively in terms of 9,10-anthraquinoid structures. Many facts support a significantly larger role for tautomeric anthraquinones than generally acknowledged [4, 5].

Natural anthraquinones are broadly used as medcinal and physiologically active preparations [3, 6]. Anthraquinones are used in practice as an important class of organic compounds in other areas such as dyes, pigments, luminophores, analytical reagents and indicators, chemicals for information storage and processing devices, catalysts and inhibitors of chemical processes, and sensitizers of photochemical reactions [6]. Therefore, studies of the role of tautomers in the chemistry of anthraquinones have become a topic of intense scientific effort.

Very important instruments for resolving this issue are electronic absorption spectra (EAS). Concurrent use of quantum-chemical calculations and correlation analysis [7] enables structural features of the compounds to be evaluated. The PPP method, which models well tautomeric equilibrium of hydroxyanthraqunones [8, 9], remains the most suitable quantum-chemical method for these purposes. According to the quantum-chemical calculations, the EAS of each tautomer contains a single π_l,π^* band. The existence of several π_l,π^* bands in experimental spectra is indicative of the presence of tautomeric equilibria.



1 - 14

1: $R_1 = R_2 = H$; **2:** $R_1 = CH_3$, $R_2 = H$; **3:** $R_1 = OCH_3$, $R_2 = CH_3$
4: R_1 = OGluc, $R_2 = CH_3$; **5:** $R_1 = OCH_3$, $R_2 = CH_2OH$
6: $R_1 = OCH_3$, $R_2 = CH_2CH_2CH_3$; **7:** $R_1 = OCH_3$, $R_2 = CH_2CH(OH)CH_3$
8: $R_1 = OCH_3$, $R_2 = CH_2COCH_3$; **9:** $R_1 = OCH_3$, $R_2 = COOH$
10: $R_1 = OH$, $R_2 = CH_3$; **11:** $R_1 = OH$, $R_2 = CH_2OH$
12: $R_1 = OH$, $R_2 = CH_2CH_2CH_2OH$; **13:** $R_1 = OH$, $R_2 = CH(OH)CH_2CH_3$
14: $R_1 = OH$, $R_2 = COOH$

Russian University of the Friendship of Nations, 117198, Moscow, ul. Miklukho-Maklaya, 6. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 411-415, September-October, 2005. Original article submitted February 28, 2005.

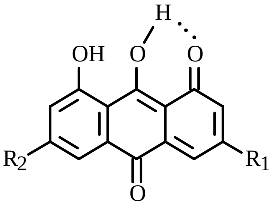
TABLE 1. Quantum-Chemical Properties of Physcion and Its Analogs

Compound	λ, nm	ΔH, eV	M, eV	E_{HOMO}, eV	E_{LUMO}, eV	E_{σ}, eV	E_{π}, eV
3	436	155.379	3.796	-8.390	-2.513	79.377	31.736
15	500	154.646	4.324	-8.053	-2.903	79.379	31.001
16	509	154.625	4.358	-7.989	-2.931	79.379	30.979
17	446	150.905	3.623	-8.232	-2.456	79.377	31.700
18	447	150.901	3.620	-8.224	-2.456	79.377	31.696
19	512	150.218	4.157	-7.905	-2.809	79.379	31.011
20	507	150.186	4.199	-7.983	-2.857	79.381	30.977
21	519	150.203	4.196	-7.850	-2.834	79.379	30.996
22	515	150.163	4.232	-7.923	-2.884	79.382	30.954
23	454	146.429	3.451	-8.111	-2.398	79.378	31.663
24	517	145.767	4.040	-7.840	-2.760	79.381	30.997
25	524	145.750	4.078	-7.788	-2.786	79.381	30.980

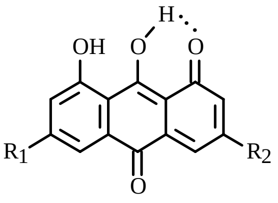
EAS in basic media are widely used in the chemistry of natural anthraquinones to establish the position of hydroxyls in the anthraquinone core [2, 3]. Therefore, data on the structures of the anions have important practical value. Also, tautomerism of hydroxyanthraquinones is conveniently studied using their ionization [8, 9].

We have previously studied tautomerism of chrysazin (**1**) and chrysophanol (**2**) [1, 9]. The present report contains results from an investigation of structurally similar compounds: physcion (**3**), frangulin A (**4**), fallacinol (**5**), compound **6**, nalgiovensin (**7**), dermoquinone (**8**), parietinic acid (**9**), emodin **10**), citreorosein (**11**), ω-rhodoptilometrin (**12**), rhodoptilometrin (**13**), and emodinic acid (**14**). Compounds **3** and **10** are the most common anthraquinones in nature.

Three tautomeric forms can exist for these compounds: 9,10-anthraquinoid (**1-14**) and two 1,10-anthraquinoids, for example for physcion (**15**) and (**16**).



15



16

Each of the three tautomers of physcion (**3**, **15**, **16**) can form two anions. Physcion can exist theoretically as a function of pH in 12 forms: three nonionized (**3**, **15**, **16**), six monoanions [1-hydroxy-6-methyl-3-methoxy-8-oxido-9,10- (**17**), 8-hydroxy-6-methyl-3-methoxy-1-oxido-9,10- (**18**), 8-hydroxy-6-methyl-3-methoxy-9-oxido-1,10- (**19**), 9-hydroxy-6-methyl-3-methoxy-8-oxido-1,10- (**20**), 8-hydroxy-3-methyl-6-methoxy-9-oxido-1,10- (**21**), 9-hydroxy-3-methyl-6-methoxy-8-oxido-1,10-anthraquinones (**22**), and three dianions [1,8-dioxido-6-methyl-3-methoxy-9,10- (**23**), 8,9-dioxido-6-methyl-3-methoxy-1,10- (**24**), and 8,9-dioxido-3- methyl-6-methoxy-1,10-anthraquinones (**25**)], Each of these is characterized by a single π_l,π^* band. At intermediate pH values, this band undergoes a smooth bathochromic shift. Compounds **5**, **7**, and **12-14** can also form anions that contain only O^- and/or COO^- in the 3- and/or 6-positions. Substituents in these positions are ionized under mild conditions. Therefore, determination of the structures of the compounds from the position of the π_l,π^* bands is not a simple matter.

We performed quantum-chemical calculations of all tautomers of physcion and its anions using the Dewar version [10] of the PPP π-electron method with varying β [11]. Table 1 lists the wavelengths λ characterizing the π_l,π^* absorption bands, the atomization energies ΔH, the solvation coefficients M, the energies of the highest occupied (E_{HOMO}) and lowest unoccupied (E_{LUMO}) molecular orbitals, and the σ- and π-bond energies (E_σ and E_π).

The experimental π_l,π^* bands were assigned by comparing the λ_{max} values with those calculated. The criterion for a correct assignment was not the closeness of these values but their linear correlation [7]. The assignments should be confirmed by several independent methods because the number of points in the correlations was minimal.

TABLE 2. Position of π_l,π^* Absorption Band of Certain 1,8-Dihydroxy-3-R_1-6-R_2-9,10-Anthraquinone Anions

R_1	R_2	Medium	λ_{max}, nm								Reference
			8,9-$(OH)_2$	$(OH)O^-$					$(O^-)_2$		
			15	17	20	19	22	21	23	25	
OCH_3	CH_3	Ethanol+AcONa	450	-	-	-	-	-		-	16
OCH_3	CH_3	Aqueous NaOH (1 N)	-	-	-	-	-	-	510	-	18
OCH_3	CH_3	Basic ethanol	-	-	-	-	-	-	512	-	13
OCH_3	CH_3	Ethanol+NaOH	-	-	503	-	-	-	-	-	19
OGluc	CH_3	Ethanol+EtONa	-	-	-	-	-	-	515	-	20
OGluc	CH_3	Ethanol+Al(III)	-	-	-	510	-	-	-	-	20
OCH_3	CH_2O^-	Ethanol+AcONa	450	-	-	-	-	-	-	-	16
O^-	CH_3	Ethanol+NH_3	-	-	502	-	-	-	-	-	21
O^-	CH_3	Aqueous NaOH (1 N)	-	-	-	-		-	520	-	18
O^-	CH_3	Aqueous NaOH (2 N)	-	-	-	-	525	-	-	-	22
O^-	CH_3	Ethanol+Al(III)	-	480	-	510	-	-	-	-	20
O^-	CH_3	Methanol+Ca(II), pH 10.5	-	-	-	-	-	553	-	-	23
O^-	CH_3	Water+Mg(II), pH 11-12	-	-	-	-	-	-	-	575	23
O^-	CH_2O^-	Ethanol+AcONa	-	-	-	-	-	-	516	-	16
O^-	COO^-	Aqueous NaOH (1 N)	-	-	-	-	525	-	-	-	18
COO^-	CH_3	Aqueous NaOH (1 N)	-	-	-	-	525	-	-	-	18
SO_3^-	SO_3^-	Water, pH 12.0	-	-	-	-	525	-	-	-	24
OCH_3	CH_3	PPP calculation	500	446	507	512	515	519	454	524	

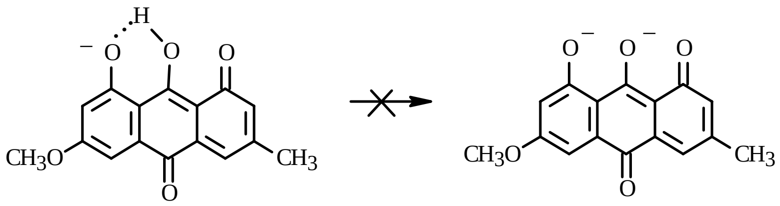
Note. Gluc = β-D-glucopyranosyl.

We previously found that the EAS of **1** [9] and **2** [1] and their anions contain π_l,π^* bands belonging not only to the 9,10- but also the 1,10-anthraquinoid structure. The known EAS for **3-14** show that they contain either one or two of these π_l,π^* bands depending on the nature of the R_1 and R_2 substituents and the medium. Thus, **3**, **9**, **10**, **14** [2], **4** [3], and **8** [12] contain a single π_l,π^* band at 430-437 nm belonging to the 9,10-tautomer; **3** [13], **5**, **10**, and **11** [14], at 450 nm (1,10-tautomer). For **3** [15], **5** [14], **6** [16], **7** [17], **11**, **13** [2], and **12** [3], both bands were found in the ranges 431-348 and 450-460 nm. Until now, this difference could not be explained. Furthermore, it undoubtedly indicates that tautomeric equilibria occur in solution.

The atomization energy ΔH characterizes the stability of a compound in the vapor phase; the solvation coefficient M, in solution. Table 1 indicates that the 9,10-states are more stable in the vapor phase; 1,10-, in solution. Ionization causes ΔH and M to decrease, i.e., the compounds are less stable.

Both hydroxyls of **3** are equivalent. Therefore, the formation of the two monoanions **17** and **18** is equally probable. This is confirmed by their practically identical ΔH and M values (Table 1). Formation of the monoanions does not prevent further ionization to the dianion **23**.

The hydroxyl in the 8-position, which is not involved in an intramolecular H-bond (IHB), in contrast with the 9-hydroxyl, is ionized first in **15** and **16**. Therefore, monoanions **19** and **21** cannot form. The H atom of the 9-hydroxyl in monoanions **20** and **22** form IHB with the 8-oxido and not with the carbonyl O atom in the 1-position because the oxido group is a better proton-acceptor; monoanions **20** and **22** are stabilized by a strong IHB that prevents dianions **24** and **25** from forming.



22 **25**

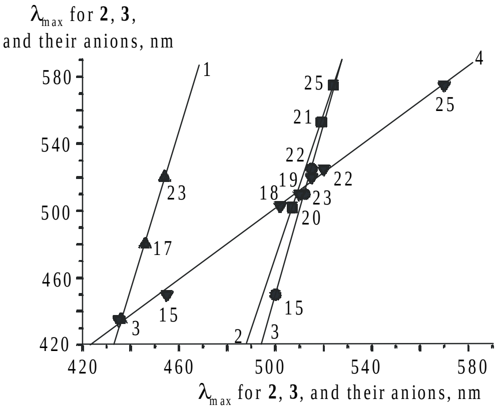


Fig. 1

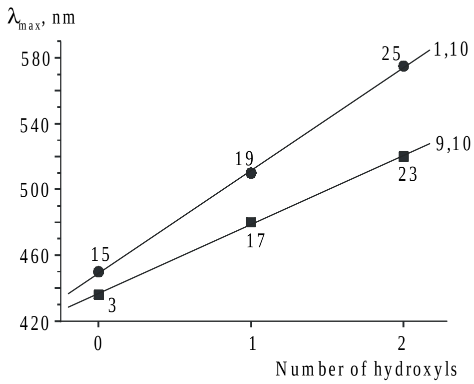


Fig. 2

Fig. 1. Correlation of experimental λ_{max} for physcion and its analogs and their anions with those calculated by the PPP method (1-3) and experimental λ_{max} for chrysophanol and its anions (4): 9,10-anthraquinones [correlation coefficient r = 0.99955, standard deviation (SD) = 1.8 nm, angular coefficient k = 4.713±0.142] (1); 1,10-anthraquinones [r = 0.99997, SD = 0.4 nm, k = 4.286±0.034 and r = 1.00000, SD = 0.0 nm, k = 5.000±0.000] (2 and 3); r = 0.9986, SD = 2.7 nm, k = 1.062±0.025 (4). Numbers of compounds correlate with those in Table 1.

Fig. 2. Experimental λ_{max} for physcion and its anions as functions of number of α-hydroxyls: 9,10-anthraquinones: r = 0.9996, SD = 1.6 nm, k = 42.000±1.155; 1,10-anthraquinones: r = 0.9997, SD = 2.0 nm, k = 62.500±1.443.

Furthermore, structures **24** and **25** are energetically unfavorable owing to the adjacent two negatively charged oxido groups. This is confirmed by their ΔH and M values, which are noticeably lower compared with monoanions **20** and **22** (Table 1).

The π_l,π^* bands of anions of physcion and its analogs were assigned (Table 2) based on this analysis and a comparison of the experimental λ_{max} values with those calculated (Fig. 1). The same was done for the experimental λ_{max} values for emodin and its anions compared with those for chrysophanol, its anions [1], and the metal complexes [15] (Fig. 2).

This assignment was confirmed by correlations of the λ_{max} values with the number of oxido groups (Fig. 3) and the sums of σ_α^A constants for hydroxyls and oxides [7] (Fig. 4).

The trends illustrated in Figs. 1-4 indicate that the 1,10-tautomers of physcion and its analogs have structure **15** whereas their ionized forms can have both structures **15** and **16**.

Table 2 shows that the overwhelming majority of known monoanions of physcion and its analogs have the 1,10-structure whereas the dianions, as a rule, are derivatives of 9,10-anthraquinone. Bands corresponding to structures **17**, **19**, **21**, and **25** could be observed only in spectra measured in the presence of complexing metal salts. Their positions agreed well with the different complexation mechanisms for hydroxyanthraquinones in neutral and basic media [5]. In neutral medium the metal ion replaces a H atom in the chelate ring of the ligand with subsequent ionization of the O–M bond. The EAS of the metal complex was identical to the spectrum of the hypothetical (impossible) anion **17** or **19** that was formed by ionization of the hydroxyl located in the chelate ring of the ligand. In basic medium, the ligand in the ionized state, in particular as the monoanion of structure **21**, forms a complex. Replacement of the H atom by the metal ion lifts the restriction on further ionization. As a result, a complex in which the ligand has the dianion structure **25** is formed.

The 9,10-dianions **23** are indistinguishable spectrophotometrically from the 1,10-monoanions **19** and **22** although the π_l,π^* band of monoanion **21** appears at longer wavelength than that of dianion **23**. These facts suggest that there is a serious error in the determination of the degree of ionization of the compounds, which can be tolerated if the existence of tautomeric conversions is not considered. For example, according to the literature [23], emodin at pH < 6.0 has λ_{max} 440 nm (nonionized form). This absorption band undergoes a bathochromic shift to 496 nm at pH 6.0-7.5. Its position does not change up to pH 10.0. This form was assigned the structure 1-hydroxy-6-methyl-3,8-dioxido-9,10-anthraquinone. Increasing the pH to 12.0 shifts the band to 525 nm. This was explained by the formation of 6-methyl-1,3,8-trioxido-9,10-anthraquinone. However, the band at 525 nm should be assigned to absorption of the 1,10-monoanion, analogous to **22**, which is consistent with tautomeric conversion of the monoanion under these conditions and not with ionization of the second hydroxyl.

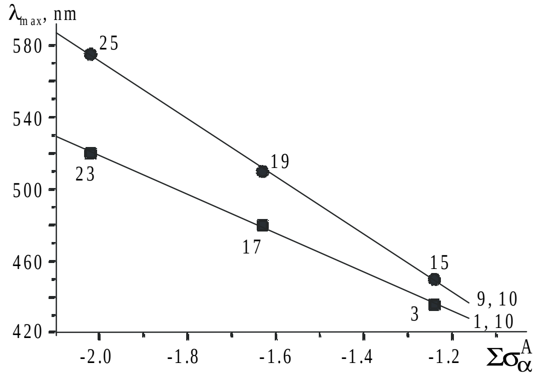


Fig. 3

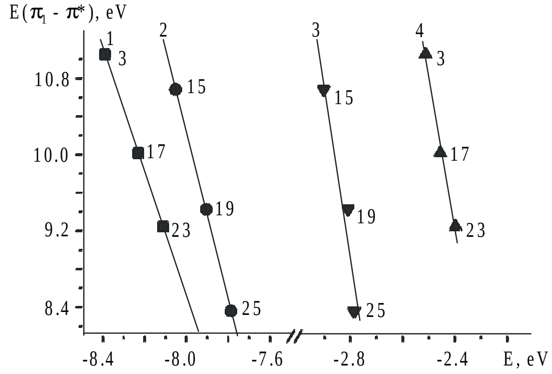


Fig. 4

Fig. 3. Experimental λ_{max} for physcion and its anions as functions of total σ_{α}^{A}- constants of hydroxyls and oxides; 9,10-anthraquinones: r = 0.9996, SD = 1.6 nm, k = -107.69±2.96; 1,10-anthraquinones: r = 0.9997, SD = 2.0 nm, k = -160.256±3.701.

Fig. 4. Correlations of π_l—π^*- transition energies for physcion and its anions with HOMO and LUMO energies: 9,10-anthraquinones (1 and 4), 1,10-anthraquinones (2 and 3), E_{HOMO} (1 and 2), E_{LUMO} (3 and 4).

Obviously the literature data for the effect of pH on the degree of ionization of hydroxyanthraquinones should be re-examined taking into account tautomeric conversions that accompany ionization.

An analysis of known EAS of 1,8-dihydroxyanthraquinone derivatives leads to two important conclusions:

1) Ionization of these compounds is accompanied by shifts of tautomeric equilibria both between 9,10- and 1,10-structures and between the two 1,10-structures **15** and **16**. Introduction of substituents in the 3- and 6-position stabilizes the 1,10-monoanions.

2) 1,10-Anions containing two α-oxido groups could not be formed at these pH values. This ionized state of the ligands was found exclusively in their metal complexes that lack an O–H...O$^-$ IHB, which prevents the second hydroxyl from ionizing.

The EAS of natural anthraquinones in all studies of our predecessors were actually examined in isolation from each other. Our work [1] was the first in which spectra of structurally similar compounds were studied together and their similarities and differences were found. Such an approach was also taken in the present study.

A comparison of the calculated λ values for chrysazin, chrysophanol, physcion, and their tautomers and anions showed that adding a methyl and then a methoxy in the 3- and 6-positions is accompanied by small bathochromic shifts of the π_l,π^* bands. Equations (1) and (2) characterize quantitatively the ratios of these shifts

$$\lambda(\text{chrysophanol}) = (0.960\pm0.030)\lambda(\text{chrysazin}) - (27.4\pm14.1)\text{ nm}, \quad (1)$$

where N = 7, r = 0.998, and SD = 2.6 nm.

$$\lambda(\text{physcion}) = (0.940\pm0.013)\lambda(\text{chrysophanol}) - (20.7\pm6.1)\text{ nm}, \quad (2)$$

where N = 12, r = 0.9992, and SD = 1.5 nm.

Moreover, the results indicate that adding a methyl and methoxyl causes shifts of certain tautomeric equilibria. For example, the bands at 480 and 553 nm, corresponding to **17** and **21**, are present in spectra of ionized chrysazin and emodin but are absent in spectra of chrysophanol anions.

The quantum-chemical parameters A, which characterize the physcion structure, change regularly upon ionization in the same way that was found for chrysophanol [1]. Thus, A changes linearly for each tautomer according to Eq. (3)

$$A = kn + A_0, \quad (3)$$

where A = λ, ΔH, M, E_{π}, E_{HOMO}, E_{LUMO}; n is the number of oxido groups, and k is the sensitivity of A to ionization.

For example, for the 9,10-anthraquinoid tautomers

$$\lambda = (9.000\pm0.577)n + (436.3\pm0.7)\text{ nm}, \quad (4)$$

where N = 3, r = 0.998, and SD = 0.8 nm.

The E_σ values practically do not change upon ionization whereas the E_π values decrease slightly according to Eq. (5)

$$E_\pi = (31.7362\pm0.0004) - (0.0365\pm0.0003)n \text{ eV}, \qquad (5)$$

where N = 3, r = 0.99997, and SD = 0.0004 eV.

This indicates that the decreased π-conjugation after ionization makes physcion less stable. The same result was found for chrysophanol [1].

Of the two monoanions, the values for **17** obey Eqs. (4) and (5) whereas those for **18** deviate slightly from the lines.

For chrysophanol, the angular coefficient k for the λ values is 11.50; for E_π values = -0.0260 [1]. A comparison of them with the coefficients k in Eqs. (4) and (5) for physcion indicates that adding a 6-methoxyl to chrysophanol causes a qualitatively different change in the sensitivity of the parameters to ionization. It decreases for λ and increases for E_π.

Linear correlations of the parameters for physcion with the E_{HOMO} and E_{LUMO} values, which characterize the ground and excited states, respectively, of the molecules indicate that both states are involved in ionization and 9,10—1,10-anthraquinoid tautomerism of physcion, like for chrysophanol. An example of this is the dependence of the π_l,π^*-transition energies $E(\pi_l—\pi^*)$, which correspond to experimental λ_{max} values, on E_{HOMO} and E_{LUMO} [Eqs. (6)-(9)].

For 9,10-anthraquinoid tautomers:

$$E(\pi_l—\pi^*) = -(6.477\pm0.055)E_{HOMO} - (43.30\pm0.45) \text{ eV}, \qquad (6)$$

where r = 0.99996 and SD = 0.011 eV;

$$E(\pi_l—\pi^*) = -(15.70\pm1.41)E_{LUMO} - (28.44\pm3.47) \text{ eV}, \qquad (7)$$

where r = 0.996 and SD = 0.115 eV.

For 1,10-tautomers:

$$E(\pi_l—\pi^*) = -(8.754\pm0.175)E_{HOMO} - (59.80\pm1.39) \text{ eV}, \qquad (8)$$

where r = 0.9998 and SD = 0.033 eV.

$$E(\pi_l—\pi^*) = -(17.98\pm5.36)E_{LUMO} - (41.44\pm15.17) \text{ eV}, \qquad (9)$$

where r = 0.96 and SD = 0.46 eV.

The r values indicate that this dependence is much more evident for the ground state than for the excited state. However, the angular coefficients for these equations indicate that the $E(\pi_l—\pi^*)$ values are more sensitive upon ionization to a change in the energies of the excited states than in those of the ground states. For 9,10-anthraquinones by 15.70:6.477 ≈ 2.4 times; for 1,10-anthraquinones, by 17.98:8.754 ≈ 2 times. The sensitivity of the $E(\pi_l—\pi^*)$ values upon 9,10—1,10-tautomerization to changes of energies of the ground states increases more (by 1.4 times) than for the excited states (by 1.15 times).

The regularity confirmed by a very large number of examples and the very high, often limiting, r values indicates that these trends are not random despite the minimal number of points.

REFERENCES

1. V. Ya. Fain, B. E. Zaitsev, and M. A. Ryabov, *Khim. Prir. Soedin.*, 119 (2005).
2. R. H. Thomson, *Naturally Occurring Quinones*, Vol. II, Academic Press, London and New York (1971); Vol. III, Chapman and Hall, London and New York (1987), p. 350.
3. R. A. Muzychkina, *Natural Anthraquinones. Bioloogical Properties and Physicochemical Characteristics* [in Russian], G. A. Tolstikov, ed., Fazis, Moscow (1998).
4. V. Ya. Fain, *Electronic Absorption Spectra and Structure of 9,10-Anthraquinones. I. 9,10-Anthraquinone and Its Monosubstituted Derivatives* [in Russian], Sputnik+, Moscow (2003).
5. V. Ya. Fain, *Electronic Absorption Spectra and Structure of 9,10-Anthraquinones. II. Disubstituted 9,10-Anthraquinones* [in Russian], Sputnik+, Moscow (2003).
6. V. Ya. Fain, *9,10-Anthraquinones and Their Use* [in Russian], Photochemistry Center of the Russian Academy of Sciences, Moscow (1999).
7. V. Ya. Fain, *Correlation Analysis of Electronic Absorption Spectra* [in Russian], Sputnik+, Moscow (2002).
8. V. Ya. Fain, B. E. Zaitsev, and M. A. Ryabov, *Zh. Obshch. Khim.*, **73**, 1688 (2003).
9. V. Ya. Fain, B. E. Zaitsev, and M. A. Ryabov, *Zh. Obshch. Khim.*, **73**, 2035 (2003).
10. M. J. S. Dewar, *Molecular Orbital Method in Organic Chemistry* [Russian translation], Mir, Moscow (1972).

11. K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **4**, 155 (1966).
12. N. K. Utkina and O. B. Maksimov, *Khim. Prir. Soedin.*, 636 (1977).
13. A. M. Tessier, P. Delaveau, and B. Champion, *Planta Med.*, **41**, 337 (1981).
14. A. Amonkar, C.-J. Chang, and J. M. Cassady, *Experientia*, **37**, 1138 (1981).
15. P. N. Verma, D. R. Lohar, and A. K. Satsangi, *Pharm. Weekbl.*, **118**, 432 (1983).
16. S. Gopolakrishnan, S. Neelakantan, and P. V. Raman, *J. Indian Chem. Soc.*, **67**, 390 (1990).
17. N. K. Utkina and O. B. Maksimov, *Khim. Prir. Soedin.*, 651 (1978).
18. J. W. Fairbairn and F. J. El-Muhtadi, *Phytochemistry*, **11**, 263 (1972).
19. M. Coskun, N. Tanker, A. Sakushima, S. Kitagawa, and S. Nishibe, *Phytochemistry*, **23**, 1485 (1984).
20. A. F. Kovalev and V. I. Litvinenko, *Khim.-Farm. Zh.*, **3**, 22 (1969).
21. H. J. Banks, D. W. Cameron, and M. J. Crossley, *Aust. J. Chem.*, **29**, 2231 (1976).
22. H. Auterhoff and S. Gedeon, *Arch. Pharm. Ber. Dtsch. Pharm. Ges.*, **304**, 241 (1971).
23. T. Pal and N. Jana, *Analyst*, **118**, 1337 (1993); A. G. Gonzalez, J. D. Martin, and C. Perez, *An. Quim. Real. Soc. Esp. Fis. Quim.*, **69**, 805 (1973).
24. H. W. Meyer and W. D. Treadwell, *Helv. Chim. Acta*, **35**, 1460 (1952).