Organometallic Chemistry

The structure of arylmercury derivatives of alizarin and their interaction with anions

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The structure of mono- and di-ArHg-derivatives of alizarin (1,2-dihydroxy-9,10-anthraquinone) and their interactions with halide- and oxygen-containing salts are examined by vibrational and electronic spectroscopy. The interaction of solid mono- and di-ArHg-derivatives of alizarin with bromides results only in the formation of the monoanion or the ion pair, depending on the nature of the counterion. Dianions are formed in a DMSO solution with very great excess of the bromide.

Key words: spectroscopy, hydroxyanthraquinones.

Works published previously[1,2] have studied the interaction of halogenides with metal-containing derivatives of phthaleins and phenolates.

In the case of metal-containing alizarin, there are additional opportunities for transformation due to two unequal metal—oxygen bonds in the molecule. In addition to the M—O bond of the phenolate type (position 2), there is an opportunity to coordinate the organometallic group with oxygen of quinoid carbonyl (metallation at position 1).

A great difference has been found previously between dissociation constants of OH-groups at positions 1 and 2. The values of pK_a (in aqueous media) are 11.8 and 7.5, respectively.[3,4] Naturally, monomercuration of alizarin, which occurs *via* the formation of the monoanion, results in the formation of the monomercuric compound at position 2.

This work presents the results of IR and UV spectroscopic studies of the structures and interactions of alizarin (**1**), its mono- (**2**), and di-mercury-containing (**3**) derivatives with halide- and oxygen-containing salts in the solid state and in solution.

Results and Discussion

In the IR spectrum of alizarin **1** measured in the solid state,[5] two bands $\nu(C{=}O)$ with participation of stretching vibrations of quinoid carbonyl were observed. They were assigned to the vibrations of the free CO-group ($\nu(C{=}O)_{free}$ 1662 cm^{-1}) and CO-group bound to the hydroxyl ($\nu(C{=}O)_{bound}$ 1631 cm^{-1}). The absorption band at 1590 cm^{-1} was assigned to the vibration of the conjugated aromatic system.

Let us analyze the spectral (IR and UV) characteristics, which were obtained for arylmercury derivatives **2** and **3** (Tables 1 and 2).

The data of the IR spectra indicate that the ArHg-group inserted at position 2 (monosubstituted derivative

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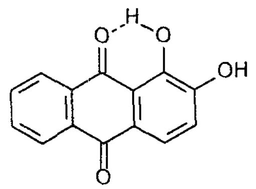
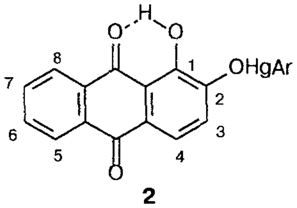


1



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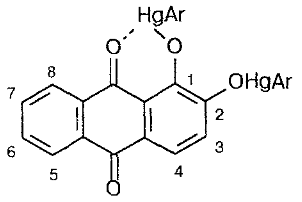

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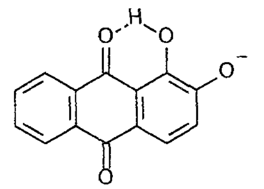
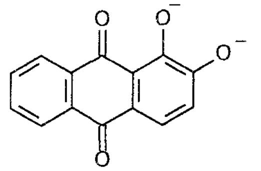


2a



3a

2) increases the conjugation in the system. The $\nu(C{=}O)_{free}$ vibration turned out to be more sensitive to the nature of the substituent at position 2 than the $\nu(C{=}O)_{bound}$ vibration: the value of $\nu(C{=}O)_{free}$ decreased by 24 cm^{-1}, while $\nu(C{=}O)_{bound}$ decreased only by 6 cm^{-1} (Fig. 1). The authors of the work[6] observed a similar change in $\nu(C{=}O)_{free}$ and $\nu(C{=}O)_{bound}$ for the insertion of ionic substituents at position 4 of the aryl ring.

In the disubstituted ArHg-derivative of alizarin **3**, the effect of the substitution approximately equally affects the $\nu(C{=}O)_{free}$ and $\nu(C{=}O)_{bound}$ vibrations. The band of $\nu(C{=}O)_{free}$ shifts to the low-frequency range by 16 cm^{-1}, while $\nu(C{=}O)_{bound}$ shifts by 18 cm^{-1} as compared with the corresponding vibrations in alizarin (Fig. 1). The difference between $\nu(C{=}O)_{free}$ and $\nu(C{=}O)_{bound}$ is 33 cm^{-1} (it is 31 cm^{-1} for alizarin). Thus, insertion of the second ArHg-group decreases $\nu(C{=}O)_{bound}$ by 12 cm^{-1} as compared with monoderivatives of alizarin.

A significant decrease in the frequency of $\nu(C{=}O)_{bound}$ shows that the ArHg-group inserted at position 1 participates, similarly to the hydrogen atom, in the formation of the cycle with the OHg...O=C coordination. (The absence of this coordination would result in the increase in the frequency and its approach to $\nu(C{=}O)_{free}$.) This cycle, similarly to the cycle with the intramolecular hydrogen bond OH...O=C, does not break in DMSO, which is indicated by the absence of differences in the spectra of compounds **1**, **2**, and **3** in the solid state and in DMSO (Table 1).

The electronic spectra in the visible range for the solid state (reflectance spectra) and DMSO solution also demonstrate an enhancement of the conjugation for

Table 1. IR spectra in the range of $\nu(C{=}O)$ in the solid state and in solutions (ν/cm^{-1})

Compound	Solid state		Solution	
	Additive	ν/cm^{-1}	Additive	ν/cm^{-1}
1	—	1662 s, 1631 s, 1590 s, 1565 sh	—	1660 s, 1634 s, 1592 s, 1574 m
	KOH	1612 m, 1574 s, 1562 sh	*t*-BuOK	1611 m, 1572 s, 1554 s
	Bu^{t}OK	1616 m, 1612 m, 1579 s, 1560 m		
2	—	1638 m, 1625 m, 1590 s, 1568 m	Bu_4NBr	1620 s, 1585 s, 1565 w
	Bu_4NBr	1624 m, 1585 s, 1550 s	*t*-BuOK	1611 m, 1572 s, 1554 s
3	—	1646 m, 1613 m, 1590 s, 1571 m	—	1645 s, 1613 m, 1588 s, 1565 m
	Bu_4NBr	1619 m, 1584 s, 1550 s	Bu_4NBr	1620 m, 1605 m, 1575 s, 1564 m

Table 2. Electronic spectra in the solid state and in solutions, λ_{max}/nm ($\varepsilon \cdot 10^{-4}$)

Compound	Solid state		Solution	
	Additive	λ_{max}/nm ($\varepsilon \cdot 10^{-4}$)	Additive	λ_{max}/nm ($\varepsilon \cdot 10^{-4}$)
1	—	436 s	—	436 (0.49)
	KOH	544 sh, 578 s, 625 sh	Bu^{t}OK	355 (0.49), 565 sh, 602 (1.08), 649 (0.97)
			Bu_4NOH	355 (0.49), 565 sh, 602 (1.1), 649 (0.9)
2	—	318 w, 483 s	—	315 m, 483 (0.54)
	KBr	335 w, 540 s	KBr	356 (0.65), 578 (0.67)
	Bu_4NBr	350 m, 410 sh, 578 s	Bu_4NOH	400 (0.27), 562 (1.02), 602 (1.75), 649 (1.15)
3	—	333 w, 518 s	—	325 (0.67), 518 (0.95)
	KBr	345 m, 415 sh, 540 s	KBr	357 m, 562 s, 602 s, 649 s
	Bu_4NBr	360 m, 420 sh, 575 s	Bu_4NOH	376 (0.28), 562 (1.06), 602 (1.75), 649 (1.77)

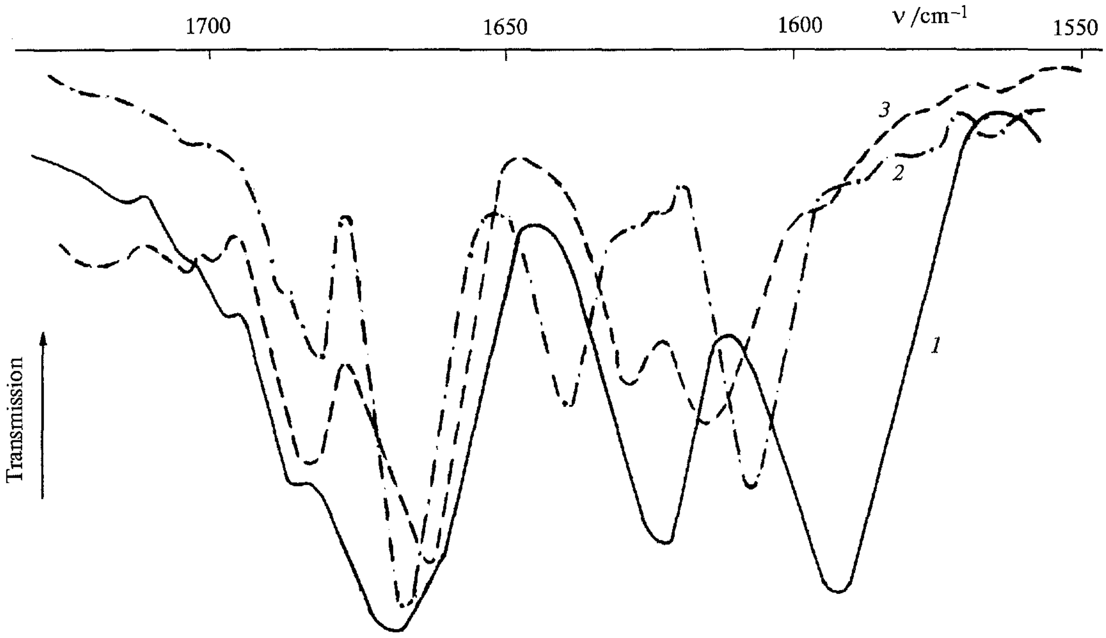


Fig. 1. IR spectra in the range of ν(C=O) in Nujol oil for alizarin (*1*); mono-ArHg-derivative (*2*); and di-ArHg-derivative (*3*).

transition from alizarin (λ_{max} 436 nm) to mono- (λ_{max} 483 nm, $\Delta\lambda_{max}$ 44 nm) and di-derivative of alizarin (λ_{max} 518 nm, $\Delta\lambda_{max}$ 74 nm) (Table 2). This sequence reflects the change in color of compounds from orange (alizarin) to cherry (monoderivative), and purple (di-derivative).

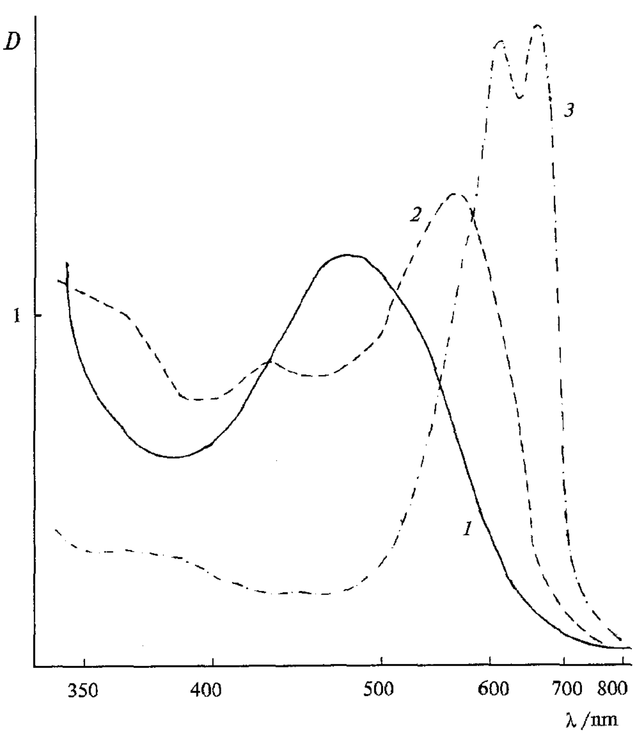


Fig. 2. Electronic spectra in DMSO for mono-ArHg-derivative of alizarin (*1*); the products of its reaction with KBr (*2*); and the products of its reaction with *t*-BuOK (*3*).

The interaction of ArHg-derivatives of alizarin **2** and **3** with bromides and chlorides in the solid state and in a DMSO solution results in (as in the case of metal-containing derivatives of phthaleins and phenolates[1,2]) ionization accompanied by a change in color. The ionization is proved by the substantial changes in the electronic spectrum in the visible range. The intensities of the initial bands decrease (483 and 518 nm), and new bands appear in the range of 560—580 and 597—649 nm (Table 2), which coincide with the bands of monoanion **2a** and dianion **3a**, respectively.[3,4] The color changes from cherry to violet and blue.

The formation of the second reaction product, arylmercury chloride, is detected for the example of the interaction with Bu_4NCl. The band at 330 cm^{-1} related to the stretching vibration of the Hg—Cl in arylmercury chloride appear in the low-frequency range of the IR spectrum.

Complexes of the studied compounds with Hal$^-$ were observed neither in the solid state nor in a DMSO solution.

It is interesting that the solid-phase reaction both for di-derivative **3** and monoderivative **2** results only in the formation of the monoanion (or of the corresponding ionic pair with K$^+$). The values of λ_{max} equal to 578 nm (or 540 nm for the ionic pair with K$^+$) are the same for the reaction products of di- and monoarylmercury derivatives with Bu_4NBr (KBr). They differ from the spectrum of the product of the solid-phase reaction of **1** with

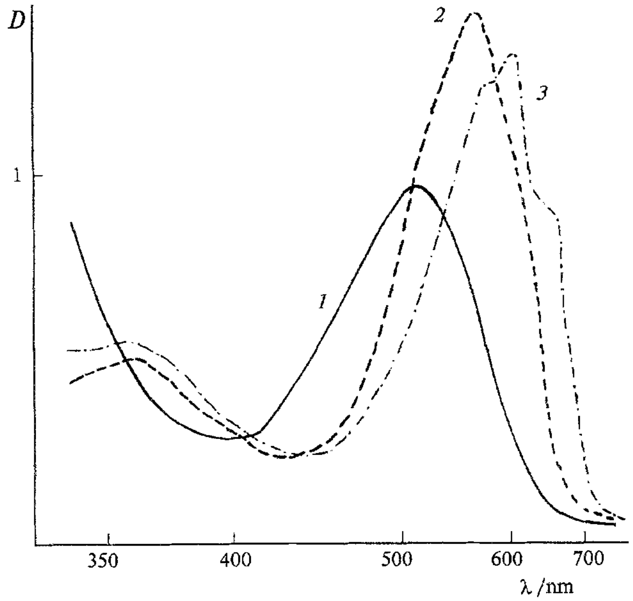


Fig. 3. Electronic spectra in DMSO of di-ArHg-derivative of alizarin (*1*); the products of its reaction with KBr (*2*) ($C_{\text{substance}} : C_{\text{Br}} = 1 : 0.5$); the products of its reaction with KBr (*3*) ($C_{\text{substance}} : C_{\text{Br}} = 1 : 200$).

KOH, which contains the band of the ionic pair of the dianion (625 nm) (Table 2) in addition to the band of the ionic pair of the monoanion (540 nm).

As should be expected, ionic pairs are not formed as a result of the interaction of compounds **1**, **2**, and **3** with anions in a DMSO solution (Figs. 2 and 3).

Naturally, the interaction of **2** with KBr or Bu_4NBr in DMSO results in the formation of the monoanion at any concentrations of Br^- (Fig. 2). At the same time, the dianion is formed when *t*-BuOK is used, because both the O—Hg and O—H bonds dissociate. We believed that the interaction of **3** with KBr or Bu_4NBr in DMSO also should easily result in the formation of the dianion. However, the monoanion is formed (blue-violet color of the solution, $\lambda_{\max}$ 578 nm) even at high concentrations of bromide ($C_{\text{compound}} : C_{\text{Br}} = 1 : 10$). Only a very large excess of Br^- results in the appearance of the dianion (color of the solution is bright blue, $\lambda_{\max}$ 602, 649 nm). A noticeable formation of the dianion was observed only at the ratio of 1 : 130. The maximum intensity of the band of the dianion was detected at the ratio of 1 : 270 (Fig. 3). It should be mentioned that the solution of the dianion in DMSO turned out to be unstable: the equilibrium shifts to the formation of the monoanion after one hour. The color of the solution changes from bright blue to blue-violet, and a hypsochromic shift of the band by 70 nm is observed in the visible range of the electronic spectrum.

IR spectra in the range of ν(C=O) are also useful for determination of the structure of the anion formed. We have found that the monoanion has the following absorption bands: 1620 s, 1585 s, and 1565 w cm^{-1}, and in the spectrum of the dianion the bands are lower by 9—12 cm^{-1}: 1611 mid, 1572 s, and 1554 s cm^{-1} (Fig. 4).

Thus, the data of the electronic and IR spectra indicate the enhancement of conjugation for transition from alizarin **1** to mono- and di-ArHg-derivatives of alizarin **2** and **3** and the existence of the chelate cycle with the intramolecular coordination CO...HgAr. The interaction with halogenides was observed both for the solid state and a DMSO solution. In the solid state both ArHg-derivatives **2** and **3** form only monoanions or ionic pairs, depending on the counterion. The dianion was detected in a DMSO solution for di-ArHg-derivative **3** only at very large excess of the bromide.

Experimental

IR spectra in the range of 4000—400 cm^{-1} were recorded on a Specord M-80 spectrophotometer, and electronic spectra were recorded on a Specord M-40 spectrophotometer. Concentrations of the compounds studied were $5 \cdot 10^{-3}$—$5 \cdot 10^{-2}$ mol L^{-1}. ^1H NMR spectra were recorded on a Bruker WP-200 (200 MHz) instrument.

1-Hydroxy-2-(4-methoxyphenylmercuroxy)-9,10-anthraquinone (2). A warm solution of 4-methoxyphenylmercury hydroxide (0.150 g, 0.46 mmol) in 15 mL of anhydrous ethanol was added to a hot solution of alizarin (0.105 g, 0.44 mmol) in 15 mL of anhydrous ethanol, and a red-violet solution formed was heated at 70 °C for 1 h in argon atmosphere. The reaction mixture was cooled and kept at 50 °C for 2 h, the formed residue was filtered off, washed with 5 mL of anhydrous ethanol and 10 mL of pentane, and then dried in a vacuum-dessicator over $MgSO_4$. Compound **2** (0.170 g, 70.5 %) was obtained as a red-violet powder. Found (%): C, 46.52; H, 2.72; Hg, 36.10. $C_{21}H_{14}HgO_5$. Calculated (%): C, 46.12; H, 2.58; Hg, 36.67. ^1H NMR spectrum (DMSO-d_6, δ, *J*/Hz): 3.75 (s, 3 H, CH_3O); 6.96, and 7.40 (AA'BB', 4 H, CH of the mercurated ring); 7.15 and 7.70 (AB-system, 2 H, H-3 and H-4, *J* = 8.5); 7.90 and 8.20 (m, 4 H, H-5, 6, 7, 8).

1,2-Di(4-methoxyphenylmercuroxy)-9,10-anthraquinone (3). Potassium methylate in methanol (5.5 mL of 0.14 *M* solution) was added dropwise to the suspension of alizarin (0.088 g, 0.365 mmol) in 15 mL of anhydrous methanol at ~20 °C in argon atmosphere. Stirring was continued for 1 h more. A solution of 4-methoxy-phenylmercuroacetate (0.281 g, 0.77 mmol) in 20 mL of anhydrous methanol was added dropwise to the deep-blue reaction mixture for 10 min, and the mixture was stirred for 8 h. The residue formed was filtered off and washed with 5 mL of methanol and 10 mL of ether, and then dried in a vacuum-dessicator over $MgSO_4$. Compound **3** (0.270 g, 87 %) was obtained as a blue-violet powder. Found (%): C, 39.69; H, 2.43; Hg, 46.13. $C_{28}H_{20}Hg_2O_6$. Calculated (%): C, 39.40; H, 2.36; Hg 46.99. ^1H NMR spectrum (DMSO-d_6, δ, *J*/Hz): 3.76 (s, 6 H, CH_3O); 6.92 and 7.46 (AA'BB', 8 H, CH of mercurated rings); 6.95 and 7.67 (AB-system, 2 H, H-3 and H-4, *J* = 8.5); 7.81 and 8.18 (m, 4 H, H-5, 6, 7, 8).

ArHg-derivatives of alizarin **2** and **3** are unstable in such solvents as C_6H_6, CH_2Cl_2, and $CHCl_3$. In these solvents, the

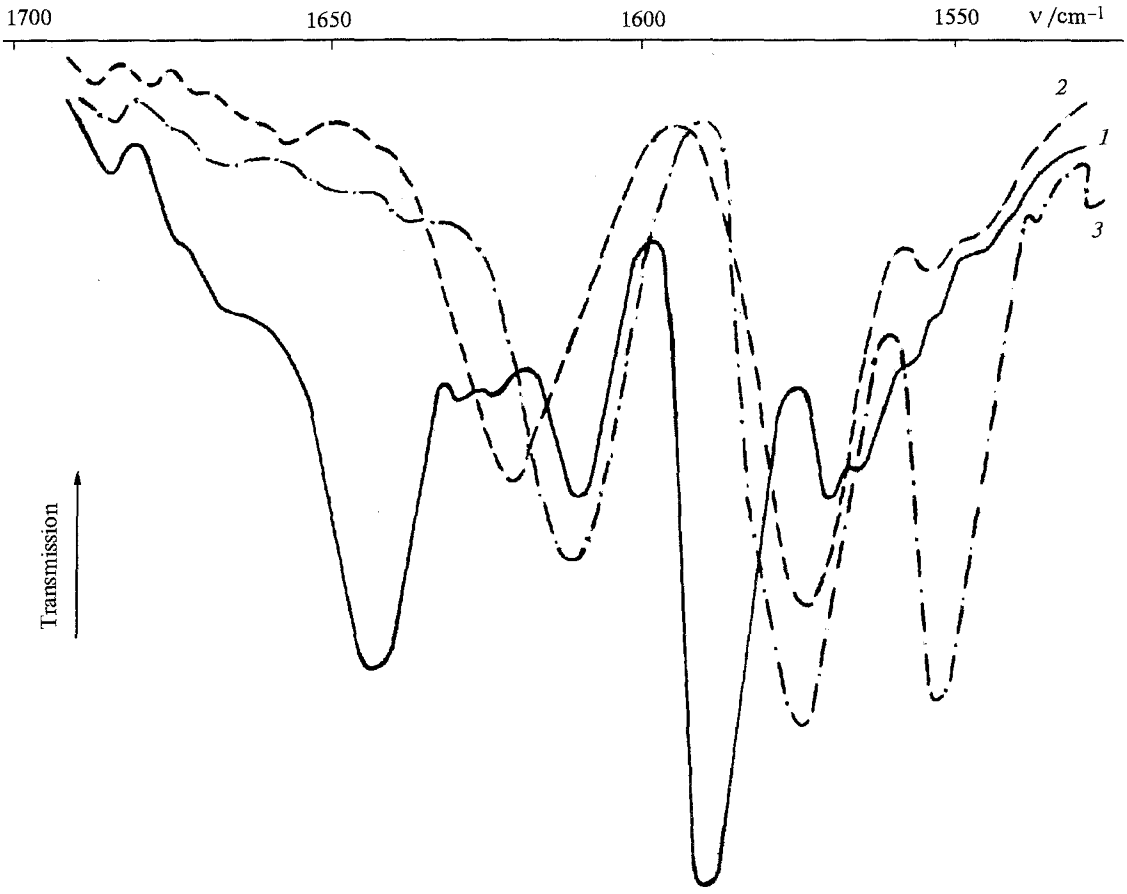


Fig. 4. IR spectra in the range of ν(C=O) in Nujol oil of di-ArHg-derivative of alizarin (*1*); the products of its reaction with Bu_4NBr (*2*); the products of its reaction with *t*-BuOK (*3*).

compounds studied rapidly decompose to alizarin, hypsochromic shifts of the bands and the change in color from cherry or purple to orange are observed. The decomposition is also noticeable from the IR spectra: the bands typical of the initial alizarin appear in the range of ν(C=O).

Solutions in DMSO are comparatively stable and can be used for measurement of the electronic and IR spectra. However, it should be taken into account that the compounds studied partially dissociate at their low concentrations in DMSO. The color of the solution deepens, and a substantial change in the electronic spectrum is observed in the visible range: the intensities of the initial bands at 483 and 518 nm decrease and a new bathochromic band appears at 560—580 nm (the absorption range of the monoanion).

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