The structure of *O*-arylmercury derivatives of dihydroxy-9,10-anthraquinones and their reactions with anions

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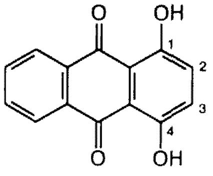
The structure of mono- and di-*O*-arylmercury-derivatives of quinizarin (1,4-dihydroxy-9,10-anthraquinone) and anthrarufin (1,5-dihydroxy-9,10-anthraquinone) and their reactions with Br^-, Cl^-, OH^-, and $^tBuO^-$ anions in the solid state and in aprotic solvents were examined by vibrational and electron spectroscopy. These reactions result in cleavage of the O—Hg bond. The formation of ions or contact ion pairs depends on the size and nature of the counterion; quinizarin dianions give very strong ion pairs with K^+ cations, which do not cleave in DMSO. The electronic structure of mono- and dianions of the compounds studied is discussed.

Key words: IR spectroscopy, electron spectroscopy, hydroxyanthraquinone derivatives.

We previously studied the reactions of *O*(*S*, *N*)-aurated and *O*(*S*, *N*)-mercurated derivatives of phthaleins,[1] nitrophenols, nitrothiophenols, and nitroanilines[2] as well as alizarin (1,2-dihydroxy-9,10-anthraquinone)[3] with salts containing Cl^- and Br^- anions by vibrational and electron spectroscopy. It was established that the reactions of the compounds studied with halide ions resulted in cleavage of a heteroatom—metal bond.

This work is devoted to studies of the specific features of the structure of mono- and disubstituted *O*-arylmercury derivatives of quinizarin (**1**) (compounds **2** and **3**) and anthrarufin (**4**) (compounds **5** and **6**) and their reactions with halide and oxygen-containing anions in the solid state and in solutions by electron and IR spectroscopy. An attempt to isolate derivatives **3** and **5** in the solid state was unsucessful; therefore, the reactions of these compounds with the anions were studied in DMSO.



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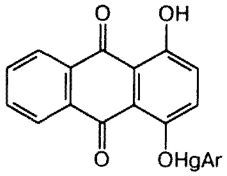

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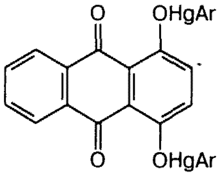

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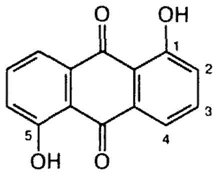

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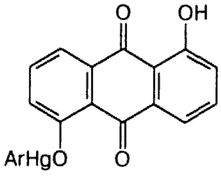

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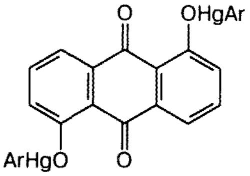

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Ar = C_6H_4OMe-4

Results and Discussion

Structure of arylmercury derivatives (2 and 6) according to IR spectroscopic data

The IR spectrum of compound **2** contains three absorption bands in the region of ν(C=O) (Table 1). The highest-frequency band at 1630—1626 cm^{-1} corresponds to vibration of the carbonyl group, which forms a hydrogen bond with the OH group, and its frequency coincides with that of the ν(C=O) band of quinizarin[4] (Fig. 1). A second band appears at 1619—1617 cm^{-1} and corresponds to vibration of the C=O group coordinated with the ArHg group. This is evidenced by its low-

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

Compound	Solid state		Solution in C_6H_6		Solution in DMSO		Compound	Solid state	
	Additive	ν	Additive	ν	Additive	ν		Additive	ν
1	—	1629 m	—	1627 m	—	1626 m	4	—	1635 s
		1590 m		1590 m		1587 m			1602 s
	KOH	1612 m	Bu^{t}OK[a]	1612 m	Bu^{t}OK	1611 m		KOH	1620 s
		1585 s	(excess)	1582 s	(excess)	1581 s			1587 s
2	—	1630 sh	—	1630 sh	—	1626 w		Bu^{t}OK	1618 s
		1617 m		1619 m		1619 m			1586 s
		1588 s		1589 s		1587 s	6	—	1618 s
	KBr	1630 m	KBr	1630 m	KBr	1628 m			1579 s
		1612 m	(excess)	1612 m	(excess)	1611 m		Bu^{t}OK	1618 s
		1585 s		1585 s		1582 s			1585 s
	Bu_4NBr	1630 m	Bu_4NBr	1626 m	Bu_4NBr	1626 m		KBr	1622 m
		1608 m	(excess)	1609 m	(excess)	1608 m			1606 m
		1581 s		1583 s		1582 s			1570 m
								KCl	1622 m
									1606 m
									1570 m
								Bu_4NBr	1618 m
									1607 m
									1569 s
								Bu_4NCl	1618 m
									1607 m
									1569 s

[a] Hereinafter, the excess is 2 and more equivalents.

frequency position. An increase in the ν(C=O) frequency should be expected in the absence of coordination, because absorption of a free CO group not bound with hydroxyl, ν(C=O), is observed in the region of 1680—1660 cm^{-1} (depending on the solvent).[5] As we showed previously,[3] replacement of the hydrogen atom by the ArHg group in an alizarin derivative resulted in a decrease in ν(C=O)$_{\text{bound}}$ by only 6—18 cm^{-1}. Hence, in the absence of such coordination, we should observe absorption in the region of 1674—1642 cm^{-1} in the IR spectrum of compound **2**. The OHg...O=C coordination in **2** is fairly strong, and the coordination bond is not cleaved on going from low-polar media to polar and strongly coordinating media. This follows from the identity of the IR spectra of this compound in the solid state, benzene, and in DMSO (see Table 1). The third band at 1589—1587 cm^{-1} is assigned to vibration of the benzene ring, ν(Ar).[3]

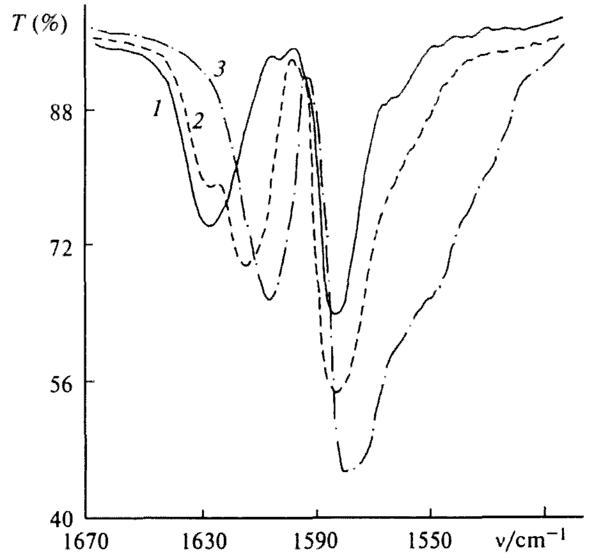
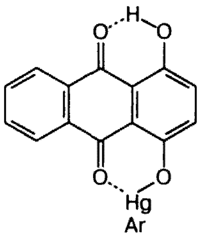


Fig. 1. IR spectra of quinizarin **1** (*1*), arylmercury derivative **2** (*2*), and product of the reaction of **2** with Bu^{t}OK (dianion) (*3*) in DMSO in the region of ν(C=O) vibrations.

The IR spectra of compound **6** in the solid state exhibit two intense bands in the ν(C=O) region: at 1618 and 1579 cm^{-1}. As can be seen from a comparison of the spectra of compounds **4** and **6**, the introduction of two ArHg groups in positions 1 and 5 results in shifting of the ν(C=O) bands by 17 cm^{-1} and of the ν(Ar) bands by 23 cm^{-1} to the low-frequency region. The decrease in the vibration frequencies is related to the formation of a coordination bond between the quinoid carbonyl and ArHg group and to an increase in conjugation due to the ArHg group, which is similar to arylmercury derivatives of other dihydroxyanthraquinones.[3] The existence of one ν(C=O) band in the spectrum of compound **6** is evidence that both carbonyls are equivalent.

Thus, the following conclusion about the structure of compounds **2** and **6** can be made on the basis of their IR spectra. Compound **2** has two chelate cycles, which are closed by both the intramolecular OH...O=C hydrogen bond and OHg...O=C coordination bond, and compound **6** contains two chelate rings with an OHg...O=C coordination bond.



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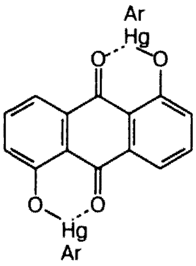

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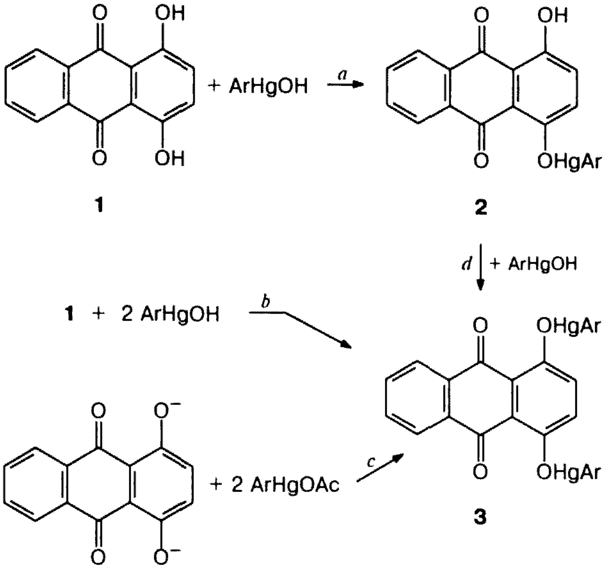
Electronic spectra

The electronic reflection and absorption spectra also demonstrate an increase in conjugation in organometallic compounds **2** and **6**, unlike initial dihydroxyanthraquinones **1** and **4**. The band with the vibrational structure in the range of 483 nm in the spectrum of quinizarin[5] (**1**) in DMSO undergoes a bathochromic shift by 32 nm* when the hydrogen atom is replaced by the ArHg group (**2**). The band in the spectrum of anthrarufin (**4**) in the region of 394—433 nm[5] is shifted by 54 nm when two hydrogen atoms are replaced by two ArHg groups (**6**) (Table 2). The complicated vibrational structure of the bands persists in the organometallic compounds, and the intensities increase by 1.5—5 times compared to those of initial compounds **1** and **4** (see Table 2).

The electronic spectra of compounds **3** and **5**, which were not isolated in the solid state, were measured in the following experiments. The spectrum of the product obtained by addition of ArHgOH (1 eq.) to a solution of quinizarin **1** in DMSO turned out to be similar to the spectrum of a solution of **2** in DMSO (Scheme 1, reaction *a*). This forced us to generate disubstituted derivative **3** by addition of ArHgOH (2 eq.) to **1** (reaction *b*) or ArHgOH (1 eq.) to **2** (reaction *d*). This resulted in the appearance of a new, more complicated band at 520—550 nm with a complex vibrational structure in the spectrum of the solution (see Fig. 2). A solution of the quinizarin dianion in the presence of ArHgOAc (2 eq.) has the same spectrum (reaction *c*). The identity of the spectra of the solutions obtained by different methods shows that derivative **3** is the product of reactions *b* and *c*, and it has absorption bands at 520—550 nm in the electronic spectrum.

A solution of compound **5** in DMSO was obtained in a similar way, and its electronic spectrum was recorded (see Table 2).

Scheme 1



Reactions with oxygen-containing anions

Dihydroxyanthraquinones were previously studied mostly in the solid state and in proton-donor solvents, and dissociation constants were obtained only for aqueous and methanolic media.[5] The electronic spectra of quinizarin **1** and its ionized forms were also studied only in proton-donor media;[6] therefore we analyzed especially the spectral changes appearing in titration of quinizarin with a solution of $\mathrm{Bu^tOK}$ in DMSO. It turned out that absorption of the monoanion in DMSO appears at 588 nm and coincides with the short-wave vibrational component of the band of the dianion (588—628 nm).[5] Unlike the dianion, the band of the monoanion has no vibrational structure. As the concentration of $\mathrm{Bu^tOK}$

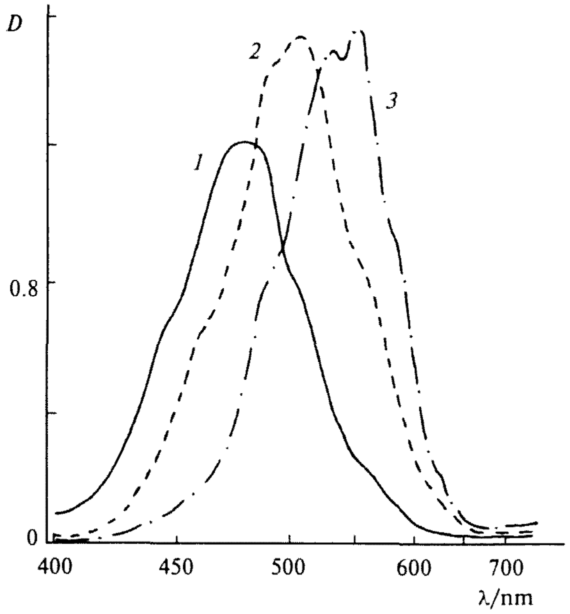


Fig. 2. Electronic spectra of quinizarin **1** (*1*), of compound **2**, the product of reaction *a* (see Scheme 1) (*2*), and of compound **3**, the product of reactions *b*—*d* (*3*) in DMSO.

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* Δλ is determined as the difference between the position of the most intense components of the vibrational structure.

Table 2. Electronic spectra in the solid state and in solutions, λ_{max}/nm ($\varepsilon \cdot 10^{-4}$/mol cm^{-1} L^{-1})

Compound	Solid state		Solution in C_6H_6		Solution in DMSO	
	Additive	λ_{max}	Additive	λ_{max} ($\varepsilon \cdot 10^{-4}$)	Additive	λ_{max} ($\varepsilon \cdot 10^{-4}$)
1	—	439 s.br	—	461 sh	—	455 sh
		526 sh		472 sh		483 (0.65)
				485 (0.67)		513 (0.39)
				503 (0.50)		
				516 (0.40)		
	KOH	568 s			KOH	547 (0.61)
		625 s			(excess)	588 (1.37)
						628 (1.90)
	Bu^{t}OK	568 s	Bu^{t}OK	581 (0.46)	Bu^{t}OK	547 sh
		625 s	(excess)	621 (0.45)	(excess)	588 s
						628 s
2	—	543 s.br	—	461 sh	—	455 sh
		588 sh		472 sh		488 (0.89)
				485 s		515 (0.95)
				505 sh		549 (0.55)
				518 sh		
	KBr	568 s.br	KBr	488 m	KBr	455 sh
		625 s	(excess)	505 sh	(excess)	485 w
				585 s		515 w
				625 s		588 s
						628 s
	Bu_4NBr	608 s	Bu_4NBr	488 w	Bu_4NBr	455 sh
		645 sh	(excess)	505 sh	(excess)	485 w
				595 s		515 w
				633 s		608 s
						645 s
3					—	490 sh
						520 s
						550 s
						588 sh
					Bu_4NBr	608 s
					(excess)	645 s
4	—	427 s			—	394 (0.61)
		455 sh				413 (0.66)
						433 (0.61)
	KOH	515 s.br			KOH	517 s
		543 sh			(excess)	546 s
	Bu^{t}OK	515 s.br			Bu^{t}OK	394 s
		543 s			(1 equiv.)	568 s
					Bu^{t}OK	517 (1.35)
					(excess)	546 (1.30)
5					—	420 sh
						439 s
						453 sh
					Bu_4NBr	394 sh
					(excess)	565 s
6	—	460 s.br			—	407 (0.52)
						467 (0.83)
						520 sh
	Bu_4NBr	397 m			Bu_4NBr	394 (0.51)
		570 s.br			(1 equiv.)	565 (1.05)
	Bu^{t}OK	515 s.br			Bu_4NBr	514 (1.33)
		543 sh			(excess)	547 (1.30)
					Bu^{t}OK	514 (1.35)
					(excess)	547 (1.31)

increases, the first and second hydrogen atoms dissociate simultaneously, which agrees with the fact that the pK_1 and pK_2 values are close.[5]

For anthrarufin **4**, there is no reliable assignment of the bands of mono- and dianions in the electronic spectra. In this connection, we studied the reaction of anthrarufin **4** with Bu^tOK in DMSO. The results of titration are presented in Fig. 3. When a small amount of Bu^tOK is added to a solution of compound **4** in DMSO, the intensity of the band of the initial anthrarufin decreases, and a new band with λ_{max} = 568 nm appears. The intensity of this band continues to increase until an equimolar ratio of concentrations of anthrarufin and Bu^tOK is achieved. The existence of the isosbestic point assumes the formation of only one product of dissociation, *viz.*, a monoanion (λ_{max} = 568 nm, violet solution). The addition of a greater than equimolar amount of Bu^tOK is accompanied by a sharp change in the electronic spectrum and, correspondingly, a change in the color of the solution from violet to pink. A band appears in the region of 517—546 nm, which has a vibrational structure typical of the dianion. Thus, we observed a very intriguing fact: the absorption band in the electronic spectrum of the anthrarufin dianion is shifted to lower wavelengths by 24—53 nm compared to the long-wave band of the anthrarufin monoanion (see Fig. 3).

Reactions of organometallic compounds **2** and **6** with KOH or Bu^tOK result in dissociation of the Hg—O bond, which is similar to dissociation of the H—O bond. For example, the reaction of oxygen-containing anions with compound **2** results in the formation of the dianion (or the corresponding ion pairs) both in the solid state and in solutions. The electronic spectrum exhibits long-wave absorption with a vibrational structure at 588—628 nm typical of the dianion. In the IR spectra, the bands at 1608 and 1581 cm^{-1} correspond to the dianion (see Fig. 1). The ν(C=O) bands of derivative **2** (1630, 1617 cm^{-1}) disappear, a low-frequency ν(C=O) band of the corresponding dianion appears instead, and the ν(Ar) band is shifted to the low-frequency region and its intensity increases.

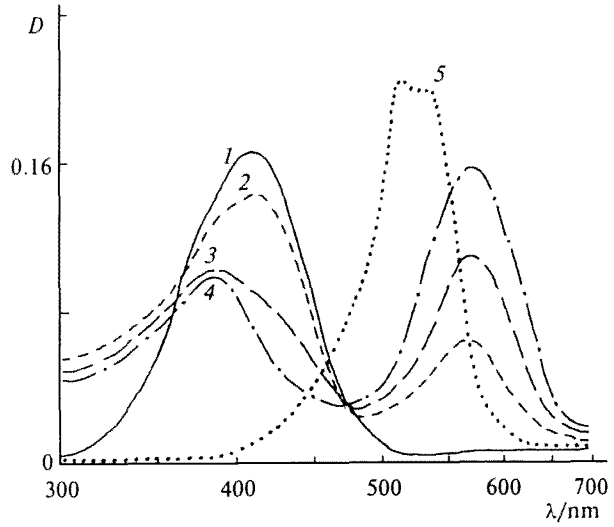


Fig. 3. Electronic spectra of anthrarufin **4** (*1*) and products of titration of **4** with a solution of Bu^tOK (*2—5*) in DMSO. The ratio of concentrations of **4** and Bu^tOK is 1 : 0.2 (*2*); 1 : 0.5 (*3*); 1 : 1 (*4*); and 1 : 2 (*5*).

The reaction of compound **6** (like that of **4**) with Bu^tOK (or KOH) results in formation of the mono- and then dianion depending on the concentration of Bu^tOK. The electronic spectra of monoanions of arylmercury derivative **6** and initial compound **4** are almost identical, λ_{max} 565 and 568 nm, respectively (see Table 2). The reaction of derivative **6** with excess Bu^tOK (or KOH), resulting in formation of the dianion, appears in the IR spectra only as a high-frequency shift of the ν(Ar) band by 6 cm^{-1} (see Table 1). Thus, the frequency of the ν(C=O) band of the dianion coincides with that of the ν(C=O) band in the spectrum of arylmercury derivative **6** (see Table 1), and the ν(Ar) band of the dianion occupies a higher-frequency position than that of compound **6**.

Reactions with halide anions

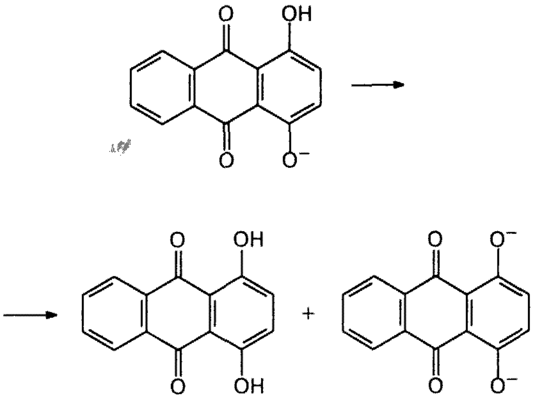
Unlike initial compounds **1** and **4**, arylmercury derivatives **2** and **6** react with halide anions. These reactions result in dissociation of the Hg—O bond to form ions or contact ion pairs similar to mercury-containing derivatives of alizarin.[3]

The dissociation of the Hg—O bond is proved by the changes in electronic and IR spectra. Reactions of **2** and **6** with Bu_4NBr, KBr, Bu_4NCl, and KCl result in strong changes in the IR spectra in the low-frequency region (400—200 cm^{-1}). In the IR spectra of the products of the reaction of **2** or **6** with Cl^- (KCl or Bu_4NCl), a new band at 324 cm^{-1} appears, which is assigned to the ν(Hg—Cl) vibration[7] and demonstrates the formation of arylmercury chloride (ArHgCl).

Other reaction products, mono- and dianions, were monitored by the electronic and IR spectra in the ν(C=O) and ν(Ar) regions. When **2** reacted with halides in the solid state and solutions (C_6H_6 and DMSO), the ν(C=O) (1617—1619 cm^{-1}) and ν(Ar) (1587—1589 cm^{-1}) bands are shifted to the low-frequency region to 1608—1612 and 1581—1585 cm^{-1}, respectively, and the intensities of these bands increased (see Fig. 1). The band at 1630 cm^{-1} assigned to the ν(C=O) vibration of the carbonyl group, which forms a hydrogen bond with hydroxyl, retains its position. Thus, based on the data from the IR spectra, it could be assumed that the quinizarin monoanion is the second product of the reactions of compound **2** with halide anions.

However, the parallel study of the electronic spectra suggests a more complicated process. The reaction of compound **2** with Hal^- in the solid state (reflectance spectra) and in solutions (DMSO and C_6H_6) is accompanied by the appearance of a new band with vibrational

Scheme 2



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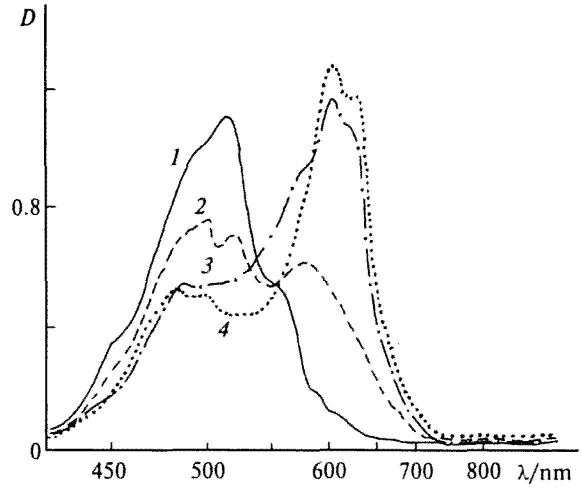

Fig. 4. Electronic spectra of the arylmercury derivative of quinizarin **2** (*1*) and products of its reaction with Bu_4NBr (*2*—*4*) in DMSO. The ratio of concentrations of **2** and Bu_4NBr is 1 : 0.2 (*2*), 1 : 1 (*3*), and 1 : 25 (*4*).

structure (588—657 nm) in the spectrum and, correspondingly, a change in color from purple to violet and blue (see Table 2). Grinding of compound **2** with KBr in the solid state (like the initial **1** with Bu^tOK or KOH) resulted in the same violet color. However, the bands in the spectra of the compounds obtained in the solid state are broad, which does not allow us to discuss the structure of the products formed. Therefore, this process was studied in detail in DMSO solutions by varying the amount of Bu_4NBr added to a solution of compound **2** in DMSO (Fig. 4). For the ratio **2** : Bu_4NBr = 1 : 0.2, the intensity of the band corresponding to compound **2** decreases, and a new long-wave band with λ_{max} = 580 nm appears. As we have already shown, this value of λ_{max} is typical of the monoanion. When compound **2** reacted with an equimolar amount of Bu_4NBr, a longer-wave band appeared, which had the characteristic vibrational structure of the quinizarin dianion (see Table 2). A band in the region of absorption of initial compound **1** (~480 nm) also appeared in the spectrum. As can be seen from Fig. 4, even a considerable excess of Br^- does not result in the disappearance of the short-wave band. It should also be mentioned that the intensity of the band of the dianion increased only until the ratio of concentrations of compound **2** and Br^- became equimolar. Further addition of the salt did not result in an increase in the intensity of the band of the dianion. This suggests that the reaction with halides resulted in the formation of three products along with ArHgHal: first, the monoanion and then the dianion and the initial quinizarin. The ratio of the dianion and the initial quinizarin was 1 : 1 when Bu_4NHal (1 equiv.) was added to **2**.* However, only the O—Hg bond, and not the O—H bond, can be cleaved under the action of Br^- in compound **2**.[1—3] Therefore, only the monoanion can be the product of this reaction. The formation of the dianion and the appearance of the initial quinizarin in the reaction can presumably be explained by disproportionation of the monoanion formed according to Scheme 2.

We found an interesting specific feature of quinizarin **1** and its arylmercury derivatives, namely, the ability to form contact ion pairs with K^+ cation in DMSO in which contact ion pairs are not usually observed.[8] Contact ion pairs did not form when alizarin and its arylmercury derivatives, studied previously, reacted with KOH and KBr in DMSO. The spectra of the products of the reactions of these compounds with KOH/KBr and Bu_4NOH/Bu_4NBr did not differ from each other.[3] Reactions of quinizarin **1** and derivative **2** with KOH/KBr and $Bu_4NOH/Bu_4NBr/Bu^tOCs$ resulted in the formation of products exhibiting different electronic spectra and different colors (Fig. 5).

As is known, the formation of ions or ion pairs depends on the size and the nature of the counterion. Since Bu_4N^+ and Cs^+ cations do not tend to form ion pairs, it is the dianion (608—645 nm, bright blue) that is the product of the reactions of compounds **1** and **2** with Bu_4NOH and Bu_4NBr/Bu^tOCs. The products of the reactions of compounds **1** and **2** with KOH and KBr are characterized by shorter absorption (λ_{max} = 588—628 nm, violet). This effect is related to formation of contact ion pairs with the K^+ cation and is observed both in the solid state and in DMSO.

Only the monoanion was obtained in the reactions of compound **6** with halides (KCl, KBr, Bu_4NCl, and Bu_4NBr) in the solid state (see Tables 1 and 2). In the presence of Bu_4NCl (Bu_4NBr), the intensity of the band in the region of ν(C=O) of the IR spectra at 1618 cm^{-1} decreases, a new band at 1607 cm^{-1} appears, and the frequency of the ν(Ar) band decreases to 1569 cm^{-1}. Thus, the bands of ν(C=O) and ν(Ar) vibrations in the IR spectrum of the monoanion are shifted by 16—

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* The calculation was based on the ε values obtained for compounds **1** and **2** and mono- and dianions (or the corresponding ion pairs).

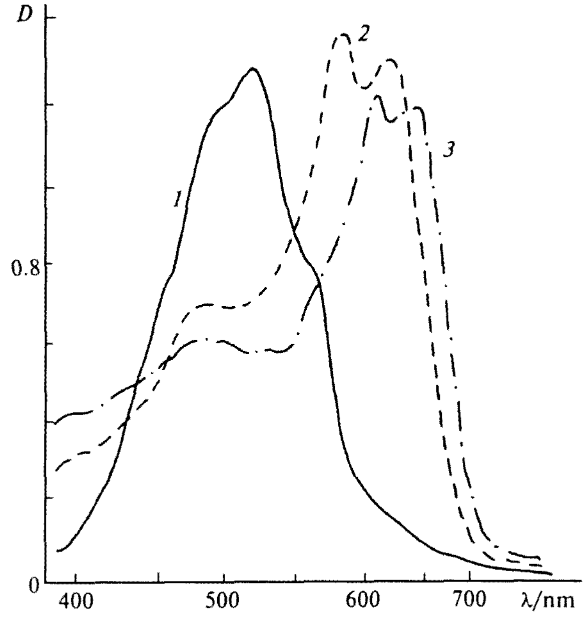

Fig. 5. Electronic spectra of the arylmercury derivative of quinizarin **2** (*1*) and products of its reactions with KBr (contact ion pair, *2*) and Bu_4NBr (anion, *3*) in DMSO.

11 cm^{-1} to the low-frequency region compared to the similar bands of the dianion. This agrees with the data in the electronic spectra and is additional evidence of an increase in conjugation in the monoanion compared to the dianion. Both the monoanion and dianion were obtained in solution (DMSO) depending on the concentration of Hal^- (see Table 2).

Comparative analysis of electronic spectra of dihydroxyanthraquinones and their arylmercury derivatives

It is of interest to compare the data from the electronic spectra of dihydroxyanthraquinones and the organometallic derivatives studied. The position of the band in the visible range makes it possible to arrange the compounds studied in the following order: 455 nm (quinizarin) > 436 nm (alizarin)[3] > 413 nm (anthrarufin) > 403 nm (1-hydroxyanthraquinone). This allowed us to draw the following conclusion: quinizarin is the most conjugated system, and for anthrarufin the conjugation of quinoid carbonyls is least and is close to the conjugation in 1-hydroxyanthraquinone. The same order can be presented for arylmercury derivatives of hydroxyanthraquinones, namely, for monosubstituted derivatives: 515 (quinizarin) > 483 (alizarin)[3] > 439 nm (anthrarufin); for disubstituted derivatives: 550 (quinizarin) > 518 (alizarin)[3] > 467 nm (anthrarufin). This sequence remains the same for monoanions of the anthraquinones studied: 588 (quinizarin) > 578 (alizarin)[3] > 568 (anthrarufin) > 554 nm (1-hydroxyanthraquinone). In the case of quinizarin and alizarin, the conjugation in the system increases even more on going to dianions, and the dianions absorb almost at the same wavelengths of 602—649 nm.[3] Unlike them, for anthrarufin the transition to the dianion results in a hypsochromic shift of the band of the dianion relative to the band of the monoanion, which is probably associated with a decrease in the conjugation in the system. Probably, this is determined by the different contributions of the ana-quinoid structure in dihydroxyanthraquinones and their anions studied. The possibility of the existence of an ana-quinoid structure for alizarin and quinizarin, a tautomer formed from 1,2- and 1,4-dihydroxyanthraquinones by transfer of hydrogen from the first hydroxyl group to the oxygen atom of the adjacent carbonyl group, is discussed in the literature,[5,9] and the electronic spectra are interpreted in consideration of this possibility.[9] However, a rigorous explanation of these facts requires quantum-chemical calculations of both the dihydroxyanthraquinones themselves and their anions.

Thus, the data from the electronic and IR spectra are evidence of a greater degree of conjugation in organometallic compounds **2**, **3**, **5**, and **6** compared to the initial quinizarin **1** and anthrarufin **4**. Compounds **2** and **5** contain two chelate rings closed by both an intramolecular OH...O=C hydrogen bond and an OHg...O=C coordination bond, and compounds **3** and **6** contain two chelate rings with an OHg...O=C coordination bond. The result of the reactions of compounds **2**, **3**, **5**, and **6** with Hal^- is cleavage of the O—Hg bond to form mono- and dianions or the corresponding ion pairs. The formation of ions or ion pairs depends on the size and nature of the counterion. A specific feature of the quinizarin dianion is the formation of very strong contact ion pairs with K^+ cation, which are not cleaved in DMSO. The electronic spectra indicate considerably lower conjugation of quinoid carbonyls in anthrarufin **4** and its arylmercury derivative **6** compared to other dihydroxyanthraquinones (quinizarin, alizarin, and their arylmercury derivatives). In the case of anthrarufin, a decrease in conjugation was observed on going from the mono- to the dianion, which is evidenced by the hypsochromic shift of the long-wave absorption band in the electronic spectrum and the high-frequency shift of the bands of ν(C=O) and ν(Ar) vibrations in the IR spectrum.

Experimental

The IR spectra were recorded on a Specord M-80 instrument in Nujol and in solutions (in CaF_2 cells, d = 0.0068—0.0620 cm, and the low-frequency IR spectra were recorded in polyethylene cells and plates).

The electronic spectra were recorded on a Specord M-40 spectrophotometer in solutions (in CaF_2 cells, d = 0.0068—0.0620 cm, and quartz cells, d = 0.1—1.0 cm) and in the solid state (using an incomplete internal reflection adapter).

4-Methoxyphenylmercury 4-hydroxy-9,10-dioxo-9,10-dihydroanthracen-1-olate (2). A solution of $4\text{-}MeOC_6H_4HgOAc$

(1 equiv.) in methanol was added to a solution of quinizarin monopotassium salt in MeOH (the salt was obtained in the reaction of quinizarin with an equivalent amount of Bu^tOK in MeOH), and the mixture was stirred for 14 h at ~20 °C in an atmosphere of Ar. The precipitate was filtered off and washed with MeOH, ether, and pentane. After drying *in vacuo*, compound **2** was obtained as a dark-violet amorphous powder in 78% yield. Found (%): C, 46.05; H, 2.62; Hg, 36.96. $C_{21}H_{14}HgO_5$. Calculated (%): C, 46.12; H, 2.58; Hg, 36.67.

This compound is unstable in CCl_4, C_6H_6, CH_2Cl_2, and MeCN. In these solvents, it gradually decomposes to the initial quinizarin **1**. Its concentrated solutions in DMSO are fairly stable. A solution in C_6H_6 was obtained in the presence of excess 18-crown-6.

Di(4-methoxyphenylmercury) 9,10-dihydro-9,10-dioxoanthracene-1,5-diolate (6). A solution of 4-MeOC_6H_4HgOAc (2 eqviv.) in methanol was added to a solution of anthrarufin dipotassium salt in MeOH (the salt was obtained by the reaction of anthrarufin with Bu^tOK (2 eq.) in MeOH). The reaction mixture was stirred for 12 h at ~20 °C in an atmosphere of Ar. The precipitate was filtered off and washed with MeOH and ether. After drying *in vacuo*, compound **6** was obtained as a carmine-red amorphous powder in 84% yield. Found (%): C, 40.28; H, 2.23. $C_{28}H_{20}Hg_2O_6$. Calculated (%): C, 39.40; H, 2.36.

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