Synthesis and physicochemical properties of 9,10-phenanthrenequinone monoxime and its nitro derivatives

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Phenanthrenequinone monoxime and its mono-, di-, and trinitro derivatives were synthesized. The acidity constants and their variation with the number and position of nitro groups were determined. The electronic and IR spectra of the nitro compounds were studied. The bands in the electronic spectra were assigned based on quantum-chemical calculations in the Pariser-Parr-Pople approximation. Correlations between the pK_a values and some calculated characteristics of the compounds under study were found.

Key words: Nitro derivatives of 9,10-phenanthrenequinone, phenanthrenequinone monoxime, 2-nitro-, 2,7-dinitro-, 2,5-dinitro-, 2,4,7-trinitrophenanthrenequinone monoxime, electronic spectra, 1R spectra, quantum-chemical calculation, acidity constants.

9,10-Phenanthrenequinone monoxime¹ is used in analytical chemistry for gravimetric² and spectrophoto-



metric³⁻⁴ determination of metal ions. Oximes of nitro derivatives of phenanthrenequinone have not been studied systematically; only random data on their structure and properties can be found in the literature.⁵⁻⁶ In this study, we synthesized a number of nitrophenanthrenequ-

inone oximes and studied their properties and structures.

Results and Discussion

Monoximes of phenanthrenequinone and its nitro derivatives can exist, like nitrosonaphthols, as two tautometric forms:



The proportions of these tautomers and their ionic forms depends on the type and positions of substituents and on the properties of the medium. Since it was impossible to grow single crystals suitable for X-ray diffraction analysis, the structures and properties of neutral and ionic monoximes were studied by IR and electronic absorption spectroscopy and by quantum-chemical calculations.

Stability of tautomers

To estimate the relative stabilities of tautomers, the heats of atomization (ΔH) for both forms of compounds 1--5 were calculated by the Pariser-Parr-Pople (PPP) method using Dewar parameters.⁷ It was found that the ΔH values for the oxime form are 1.001--0.630 eV greater than those for the nitroso tautomer (Table 1). This implies that compounds 1-5 exist in the oxime form. As the number of nitro groups in the phenan-threne nucleus increases, the relative stability of the oxime form decreases. The slight difference between the ΔH values for the oxime and its anion with allowance for the energy of the O--H bond accounts for the fairly easy dissociation of the NO--H group.

IR absorption spectra

The oxime forms of compounds 1-5 can be characterized using the bands of the stretching vibrations of the

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Table 1. Results of the calculation of the energy of atomization (ΔH) , the energy of π -bonds $(E\pi)$, solvation coefficients (M), dipole moments (μ), and $E_{\text{HOMO}}/E_{\text{LUMO}}$ energies of compounds 1--5

Compound		<u>Δ</u> <i>H</i>	Επ	М	μ	$E_{\rm HOMO}/E_{\rm LUMO}$
_			eV		/D	/eV
1	A	136.407	26.103	1.379	1.402	-9.104/-2.750
	B	131.942	26.078	1.249	1.214	~8.820/-2.676
	С	135.406	25.149	1.984	5.247	-8.883/-3.050
2	А	138.384	30.095	5.347	4.011	-9.412/-3.682
	B	133.952	30.100	5.181	3.987	-9.050/-3.619
	С	137.705	29.440	5.304	9.038	-9.117/-3.607
3	A	140.790	33.577	8.978	1.333	-9.679/-4.016
	B	136.369	33.591	8.812	1.876	-9.289/-3.942
	С	140.109	32.915	8.910	3.876	-9.441/-4.085
4	A	140.856	33.628	9.026	5.905	-9.584/-3.942
	B	136.429	33.639	8.861	6.336	-9.206/-3.856
	С	140.135	32.931	8.925	9.719	-9.344/-3.989
5	A	143.197	37.045	12.606	4.468	-9.914/-4.374
	B	138.785	37.068	12.440	5.323	-9.512/-4.295
	С	142.551	36.416	12.561	2.771	-9.671/-4.411

Note: A is oxime, B is the oxime anion, C is the nitroso form.

oxo groups (Table 2). The IR spectra of compounds 1-5 in the crystalline state (pellets with KBr) exhibit the v(C=O) mode in the 1652-1685 cm⁻¹ range.

In the case of compounds 1 and 2, the v(C=O) bands in the spectra of solid samples are shifted by ~10 cm⁻¹ to higher frequencies from the v(C=O) values of the corresponding quinones containing no hydrogen bonds (see Table 2). It can be suggested that the C=O

groups in compounds 1 and 2 do not form hydrogen bonds. The diffuse absorption band corresponding to the stretching vibrations of the O—H group observed at ~2200-3400 cm⁻¹ arises due to intramolecular hydrogen bonds (IHB) formed according to the A fashion without participation of the oxo group. Stability of this six-membered ring is due to the fact that the oximegroup nitrogen atom is more basic than the oxo group.

The v(C=O) bands in the spectra of solid compounds 3-5 are shifted to lower frequencies from the v(C=O) modes of analogous quinones by 17-48 cm⁻¹. In these compounds, the oxo group may be involved in the formation of IHB of type **B**.

The existence of IHB in the crystals of compounds 1-5 is consistent with the fact that the v(C=O) values change on dissolution of solid samples in 1,2-dichloroethane. In the spectrum of a dilute solution of compound 1, the v(C=O) mode shifts to lower frequencies by 25-45 cm⁻¹ (see Table 2), whereas in the spectra of solutions of the corresponding 9,10-phenanthrenequinones, only a slight high-frequency shift is observed. Apparently, on dissolution of 1, the intermolecular hydrogen bonds are cleaved and intramolecular hydrogen bonds of the =NOH-O=C type are formed instead.

The assignment of the v(N=C) bands is difficult, because this region is overlapped by a number of bands corresponding to the aromatic rings. The symmetrical $v_s(NO_2)$ and antisymmetrical $v_{as}(NO_2)$ frequencies of the stretching vibrations of nitro groups are in good agreement with these values for the corresponding nitro derivatives of 9,10-phenanthrenequinones.

Com-	v/cm ⁻¹						
pound	C=0	0H	C=N, C=C	NO _{2as, s}			
1	1680 s (1655 w, 1633 m)*	2200-3400 (2800)	1600 s 1555 w				
2	1685 s	2200—3400 (2800)	1614 m 1595 s, 1572 w	1525 vs 1350 vs			
3	1665 s	1800-3100 (2450)	1617 w, 1608 s 1570 m	1518 vs 1345 vs			
4	1675 s	2000—3500 (2750)	1613 w, 1595 m 1575 m	1515 vs 1340 vs			
5	1652 m	1910-3450 (2680)	1600 s 1575 w	1520 m 1350 vs			
9,10-P anthrei	'hen- 1670 s ne- (1680 s)** ne		1592 s	-			

Table 2. IR spectra of compounds 1-5 in the crystalline state (pellets with KBr)

Note: vs is very strong, s is strong, w is weak, m is medium. The average v(OH) frequencies are given in parentheses.

* v(C=0), in solution in $C_2H_4Cl_2$. ** v(C=0), in solution in CCl_4 .



Electronic absorption spectra

An independent conclusion concerning the tautomeric form of compounds 1-5 was drawn from analysis of electronic spectra. The nitroso group is known to be responsible for a band due to the electronic transition at 560-670 nm.⁹ The electronic spectra of the compounds under study in the crystalline state and in solutions in ethanol, acetonitrile, and $C_2H_4Cl_2$ do not exhibit this band but instead, they contain bands in the region of 200-400 nm, which are related to the oxime form. Thus, electronic absorption spectroscopy does not permit detection of the nitroso form of these compounds.

To assign bands in the electronic spectra of compounds 1-5, quantum-chemical calculations by the PPP method were carried out.⁷ The calculated absorption frequencies are in satisfactory agreement with experimental data (Fig. 1). The long-wavelength electronic transition in the electronic spectrum of compound 1 corresponds to $\lambda = 349$ nm and is due (by 90%) to the transfer of π -electron density from the highest occupied molecular orbital Ψ_m (HOMO) to the lowest unoccupied molecular orbital Ψ_m (LUMO). The second calculated band, $\lambda = 321$ nm, is due (by 72%) to the Ψ_{n-1} $\rightarrow \Psi_m$ transition.

In the experimental spectrum, these transitions are matched by a broad $\pi \rightarrow \pi^*$ band at -320-370 nm, which is apparently partially overlapped by the $n \rightarrow \pi^*$ band of the C=O group. The molecular diagrams of the ground and the first excited states show that the longwavelength transition involves the transfer of π -elec-



Fig. 1. Electronic absorption spectrum of compound 4 in ethanol $(5 \cdot 10^{-5} \text{ mol } L^{-1}; V = 40 \text{ mL})$ recorded during titration with a solution $(10^{-2} \text{ mol } L^{-1})$ of NaOH (1-5). Volume NaOH/mL = 0 (1), 0.24 (2), 0.08 (3), 0.12 (4), 0.16 (5). The vertical lines show the calculated electronic spectrum of neutral (continuous) and anionic forms (dashed) of compound 4; the dependence of the optical dencity ($\lambda = 424$ nm) on pH of the solution.

tron density mainly from all the carbon atoms to oxygen of the oxo group and nitrogen of the oxime group.

According to calculations, the most intense band in the experimental spectrum, $\lambda_{\max} = 260$ nm, is matched by two electron transitions, $\lambda = 254$ nm, $\Psi_{n-2} \rightarrow \Psi_m$ (26%), $\Psi_n \rightarrow \Psi_{m+1}$ (25%), $\Psi_n \rightarrow \Psi_{m+2}$ (24%); $\lambda = 249$ nm, $\Psi_n \rightarrow \Psi_{m+1}$ (32%), $\Psi_{n-3} \rightarrow \Psi_m$ (25%), $\Psi_{n-1} \rightarrow \Psi_{m+1}$ (17%). The observed band $\lambda_{\max} = 231$ nm corresponds to three electron transitions ($\lambda = 240$, 230, and 227 nm).

In the electronic spectrum of compound 1 recorded in an alkaline medium, the long-wavelength band undergoes a bathochromic shift to 403 nm, the band at 231 nm becomes much less intense, while the band at 260 nm becomes more intense (Table 3). The low-intensity bands at about 320-370 nm are overlapped by other bands. According to calculations, the long-wavelength band in the spectrum of the anion derived from compound 1 is shifted bathochromically from the longwavelength band in the spectrum of neutral oxime by 27 nm. It corresponds (by 94%) to an electronic transition from the HOMO (Ψ_n) to the LUMO (Ψ_m) . This is in satisfactory agreement with the experimental data according to which $\Delta_{max} = 30$ nm. It follows from the molecular diagrams of the ground and the first excited states of anion 1 that this transition involves displacement of the electron density $\Delta q = 0.290$ e from the C=O group to the rest of the molecule.

Compound		$\lambda_{max}/nm \ (log \epsilon)$					
		λ ₁	λ ₂	λ3	λ ₄		
1	A	231	260	317	373		
		(4.35)	(4.51)	(3.75)	(3.60)		
	B		257	359	403		
			(4.60)	(3.78)	(3.90)		
2	A	240	275	321 sh	370 sh		
		(4.27)	(4.20)				
	B		281	345	417		
			(4.35)	(3.95)	(3.94)		
3	A	229	281	325	374 sh		
		(4.32)	(4.28)	(4.18)			
	B	234	285	345	446		
		(4.23)	(4.47)	(4.15)	(3.95)		
4	A	229	273	327			
		(4.52)	(4.34)	(4.15)			
	B	231	276	336 sh	424		
		(4.45)	(4.49)		(3.98)		
5	A	238	276	324			
		(4.37)	(4.24)	(4.12)			
	B	236	280	336 sh	463		
		(4.31)	(4.41)	(4.11)	(3.76)		

 Table 3. Electronic absorption spectra of compounds

 1-5 in EtOH and EtOH + NaOH

Note: A is oxime, B is the oxime anion.

For compounds 1-5, the intensity of the λ_1 bands decreases with an increase in the pH of the solutions, whereas the intensity of the λ_2 bands increases (see Table 3, Fig. 1). The long-wavelength bands of the anionic species in the electronic spectra of the studied compounds shift bathochromically as the number of nitro groups in the phenanthrene nucleus increases.

The measured pK_1 values for compounds 1-5 (10.61, 9.02, 8.60, 8.10, and 6.50, respectively) depend on the number and positions of the nitro groups in the molecules of 9,10-phenanthrenequinone monoximes. Thus the introduction of a nitro group in position 2 (compound 2) results in a decrease in the pK_a value by 1.59 with respect to compound 1, which can be explained by the inductive effect of the substituent. When the second nitro group is introduced into position 7 or 5 (compounds 3, 4), the pK_a value decreases by 0.42 and 0.92, respectively, with respect to that of compound 2: The introduction of a nitro group into position 4 (compound 5) decreases the pK_a by 2.10 in relation to this value for compound 3. The observed changes indicate that nitro groups located in the benzene ring closest to the oxime group have a substantially greater influence on the pK_{a} values of the corresponding oximes. In addition, the nitro groups in positions 4 and 5 influence the acidity of oximes somewhat more strongly than these groups in positions 2 and 7, respectively. The charges of the nitrogen and oxygen atoms of the oxo and oxime groups, calculated in terms of the π -electron approximation,

depend slightly on the positions and the number of nitro groups in compounds 1-5. This might be due to the fact that the predominant inductive effect of nitro groups on the oxime group is not adequately taken into account in the PPP method.

Intermolecular interactions should also have a certain effect on the pK_a values. Indeed, a linear correlation between the calculated solvation coefficients (*M*), which take account of the electrostatic interaction of the molecule with the solvent, and the pK_a values of compounds 1-5 was found, M = 31.3-2.8, pK_a (r = 0.97). Thus, the inductive effect of the nitro groups and intermolecular interaction are the crucial factors determining the pK_a values of compounds 1-5.

Experimental

The IR spectra in the 4000-400 cm⁻¹ range were recorded on a Specord IR-75 spectrophotometer for crystalline samples (as pellets with KBr) and in solution (dichloroethane). The electronic absorption spectra in the 200-700 nm range were measured on Specord M-40 and Specord UV-VIS spectrophotometers in solution in EtOH, MeCN, and C₂H₄Cl₂. The acidity constants (K_{n}) were determined by pH-metric titration of alcoholic solutions of compounds 1-5 with an aqueous solution of NaOH with simultaneous recording of electronic spectra, according to the procedure reported in a known study.¹⁰ The purity of compounds 1-5 was checked and $R_{\rm f}$ values were determined by TLC on Silufol UV-336 plates in the benzene-acetone (10 : 1) system. Quantum-chemical calculations were carried out by the PPP method with optimization of interatomic distances based on the minimum atomization heats.⁷ The data of crystal optical analysis indicate that the isolated compounds are single-phase materials.

The monoximes were synthesized from phenanthrenequinone ("chemically pure" grade). The nitro derivatives, 2-nitrophenanthrenequinone¹¹ and 2,7-dinitro-,¹² 2,5-dinitro-,¹² and 2,4,7-trinitrophenanthrenequinone,¹² were prepared by known procedures.

Phenanthrenequinone monoxime (1) was synthesized by a modification of a known procedure¹: phenanthrenequinone (6.0 g, 29 mmol) and NH₂OH \cdot HCl (2.5 g, 36 mmol; a 1.24-fold excess) were refluxed in a mixture of 90 mL EtOH and 15 mL of chloroform for 45 min. The crystals that precipitated after cooling the reaction mixture were filtered off, washed with ethanol and water, and dried in air to a constant weight to give 5.0 g (yield 77.8%) of compound 1, m.p. 156–159 °C (from ethanol) (cf. Ref. 1, m.p. 158 °C), pK. 10.61, R = 0.82

(from ethanol) (cf. Ref. 1, m.p. 158 °C), pK_a 10.61, $R_f = 0.82$. **2-Nitrophenanthrenequinone monoxime (2).** A mixture of 2-nitrophenanthrenequinone (3.0 g, 12 mmol) and NH₂OH · HCl (3 g, 43 mmol; a 3.6-fold excess), ethanol (120 mL), and chloroform (20 mL) was refluxed for 50 min. After cooling the reaction mixture, the precipitate was filtered off, washed with ethanol and water, and dried to a constant weight to give 2.5 g (yield 78.6%) of compound 2, m.p. 202-204 °C (from a mixture of AcOH and 1,4-dioxane). Found (%): C, 62.65; H, 2.89; N, 10.24. $C_{14}H_3N_2O_4$. Calculated (%): C, 62.69; H, 2.99; N, 10.43; pK_a 9.02, $R_f = 0.71$.

2,7-Dinitrophenanthrenequinone monoxime (3). A suspension of 2,7-dinitrophenanthrenequinone (2.0 g, 7 mmol) and $NH_2OH \cdot HCl$ (1.2 g, 17 mmol; a 2.4-fold excess) was refluxed

for 70 min in 30 mL of isopropyl alcohol. The precipitate was filtered off, washed with isopropyl alcohol and water to a neutral pH, and dried to a constant weight to give 1.76 g (yield 83.8%) of compound 3, m.p. 217–220 °C (from 1,4-dioxane). Found (%): C, 54.49; H, 3.03; N, 14.05. $C_{14}H_7N_3O_6$. Calculated (%): C, 53.62; H, 2.24; N, 13.42; pK_a 8.60, $R_f = 0.45$.

2,5-Dinitrophenanthrenequinone monoxime (4). A mixture of 2,5-dinitrophenanthrenequinone (1.0 g, 34 mmol) and NH₂OH · HC1 (0.3 g, 43 mmol; a 1.27-fold excess) was refluxed for 30 min in 15 mL of isopropyl alcohol. The precipitate (formed after 6–7 h) was filtered off, washed by isopropyl alcohol and water to a neutral pH, and dried in a desiccator to give 0.6 g (yield 57.1%) of compound 4, m.p. 206–208 °C (from 1,4-dioxane). Found (%): C, 52.81; H, 3.16; N, 12.93. C₁₄H₇N₃O₆. Calculated (%): C, 53.62; H, 2.24; N, 13.42; pK_a 8.10, $R_{\rm f} = 0.55$.

2,4,7-Triuitrophenanthrenequinone monoxime (5). A mixture of 2,4,7-trinitrophenanthrenequinone (0.5 g, 15 mmol) and NH₂OH · HCl (0.15 g, 22 mmol; a 1.5-fold excess) was refluxed in 20 mL of isopropyl alcohol for 20 min. After cooling, the reaction mixture was diluted with water in a ratio of ~1 : 2. After 24 h, the precipitate was filtered off and dried in a desiccator to give 0.4 g (yield 76.9%) of compound 5, m.p. 152-154 °C (twice from AcOH). Found (%): C, 46.74; H, 1.79; N, 15.45. $C_{14}H_6N_4O_8$. Calculated (%): C, 46.93; H, 1.68; N, 15.64; pK_a 6.50, $R_f = 0.57$.

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