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MOLECULAR-ORBITAL SELF-CONSISTENT FIELD CALCULATIONS OF QUINOLINE AND ITS DERIVATIVES.

II.* CALCULATION OF THE ELECTRONIC STRUCTURE AND SPECTRA OF 8-MERCAPTOQUINOLINE

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The electronic spectra of the thiol, anionic, protonated, and mesoionic forms of 8-mercaptoquinoline and the mesoionic form of 5-mercaptoquinoline and the 5-mercapto-N-methylquinolinium ion were calculated within the CNDO (complete neglect of differential overlap) approximation. The inclusion of the d orbitals of the sulfur atom in the AO basis has virtually no effect on the energies of the electron transitions of these compounds.

In the present research we calculated the various forms of 8-mercaptoquinoline in order to ascertain the electronic structures and nature of the electron transitions and to compare them with the analogous data for 8-hydroxyquinoline.

The spectral properties of these compounds are also of interest in connection with the problems of the structures of the chelate compounds of 8-mercaptoquinoline and 8-hydroxyquinoline. On the basis of electronic absorption spectra it has previously been assumed [1] that the ligands in 8-mercaptoquinoline complexes of nontransition metals have structures analogous to the thiol form, whereas the ligands in the corresponding complexes of transition metals have structures analogous to the mesoionic form of the reagent.

The thiol (I), anionic (II), cationic (III), and mesoionic (IV) forms of 8-mercaptoquinoline and the mesoionic form of 5-mercaptoquinoline (V) and the 5-mercapto-N-methylquinolinium cation (VI) were calculated within the CNDO (complete neglect of differential overlap) approximation (with an sp basis for the AO). Twenty-five lower singly excited configurations were taken into account in the calculation of the electronic spectra. The $u_{\mu\mu}$ and γ_{AA} values were borrowed from [2], and the β_A° values were varied for reproduction of the electronic spectra of the thiol and mesoionic forms of 8-mercaptoquinoline (β_H° = −12, β_C° = −16, β_N° = −24, and β_S° = −18 eV). The contribution of the d orbitals of the sulfur atom to the formation of the bonds was examined in the case of the thiol and mesoionic forms of 8-mercaptoquinoline (with an spd' basis for the AO of the sulfur atom).

The u_{dd} value was calculated from the data in [3], and the β_{AB}° (d) value for the orbitals was calculated on the basis of β_{AB}° (d) = $0.5\beta_{AB}^\circ$ (sp). The two-center two-electron integrals were calculated from the Mataga formula. The geometry of the molecules was selected in accordance with the data in [4], the C—S and S—H bond lengths were 1.75 and 1.35 Å, respectively, and the CSH angle was 100°.

The observed and calculated energies and oscillator forces of the singlet—singlet electron transitions of I-VI are compared in Table 1. In the case of the thiol form of 8-mercaptoquinoline the calculation satisfactorily conveys the energies of the electron transitions and the oscillator forces, which correspond to α + p, β, and β' transitions (π—π^* bands) of quinoline and 8-hydroxyquinoline. An n—π^* band is not observed in the spectrum because of overlapping with the intense π—π^* absorption.

*See [4] for communication I.

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The ionized and mesoionic forms of 8-mercaptoquinoline are of interest from the point of view of elucidation of the nature of the electron transitions and the electronic structures [5]. The calculation satisfactorily conveys the changes in the electronic spectrum on passing from the thiol form to the charged forms of 8-mercaptoquinoline (Table 1). Protonation of the nitrogen atom leaves the position of the α band virtually unchanged, whereas the p band is shifted to the long-wave region. In the formation of the anionic form of 8-mercaptoquinoline the p band also undergoes a pronounced bathochromic shift. A comparison of the other transitions is impossible, since excited states of the α and β types cannot be isolated in the spectrum of the anionic form.

The energy of the long-wave transition of the mesoionic form in polar solvents, the molecules of which do not contain a hydroxy group (the mesoionic form is not formed in nonpolar solvents), is also satisfactorily conveyed. For example, in bromobenzene the energy of this band is 2.12 eV, as compared with the calculated value of 1.86 eV.

However, a comparison of the remainder of the absorption spectrum with the calculated data is impossible, since only ~1% of the mesoionic form is generated in these solvents. The bands of the mesoionic form are masked by the absorption of the thiol form. In hydroxy-containing solvents (for example, in water, in which 100% of the mesoionic form is present [5]) the absorption bands of the mesoionic form undergo a pronounced hypsochromic shift, as a consequence of which these data are not suitable for comparison with the results of the calculation. The spectrum of the 8-hydroxy-N-methylquinolinium ion in chloroform [4] was selected as a standard in the calculation of the electronic spectrum of the mesoionic form of 8-hydroxyquinoline. However, in the case of 8-mercaptoquinoline the corresponding analog — the 8-mercapto-N-methylquinolinium ion — is not formed because of steric hindrance. The spectrum of the 5-mercapto-N-methylquinolinium ion (100% of the mesoionic form in organic solvents) was selected as the standard in this case. The changes in the absorption spectrum of this compound on passing from water to polar solvents that do not contain hydroxy groups are similar to the changes in the case of the mesoionic form of 8-mercaptoquinoline.

According to the data in Table 1, the calculation satisfactorily conveys the electron transitions of the 5-mercapto-N-methylquinolinium ion in chloroform. Considering the above, it may be assumed that the calculation also models the electronic spectrum of the mesoionic form of 8-mercaptoquinoline in solvents that do not contain a hydroxy group (compare the long-wave bands observed in the case of bromobenzene, acetone, etc. in Table 1 and [5]).

The long-wave absorption in the mesoionic form corresponds to a single configuration π—π^* transition of the p type.

The large bathochromic shift of this band relative to the thiol form is due to the overall effect of protonation of the nitration atom and the formation of a negative charge on the sulfur atom (compare the calculations of the anionic and protonated forms of 8-mercaptoquinoline). The transition at 1.86 eV is accompanied by transfer of 0.6 e of charge from the $3p\pi$ orbital of the sulfur atom to the quinoline ring (the charge-transfer band and the analogy with the p band of quinoline are actually extremely arbitrary); there is a substantial change in the dipole moment of the molecule from ~13 D in the ground state to ~5 D in the first excited state. This explains the hypsochromic shift of the long-wave band in the spectrum of the mesoionic form of mercaptoquinolines on passing to more polar solvents.

According to the results of the calculation, the dipole moment of the mesoionic form in all of the excited states is lower than that in the ground state, and all of the calculated electron transitions should consequently have lower energies as compared with the spectrum of the compound in water (Table 1). The magnitude of the shift is determined both by the dipole moment of the molecule in the ground and excited states and by the characteristics of the solvent (ε and n). In conformity with this, the differences between the calculated and experimental spectra should be maximal in weakly polar solvents that do not contain a hydroxy group (compare the spectra of the 5-mercapto-N-methylquinolinium ion and the 8-hydroxy-N-methylquinolinium ion in chloroform, Table 1 and [4]).

To shed some light on the problem of the effect of the d orbitals of the sulfur atom on the results obtained in this study we calculated the thiol and mesoionic forms of 8-mercaptoquinoline in an spd' basis for the sulfur atom. According to the data in Table 1, this has virtually no effect on the electron transitions of these compounds (in comparison with the sp basis). The populations of the d orbitals are 0.21 and 0.09 e, and the increase in the charge on the sulfur atom as compared with the sp basis are 0.09 and 0.05 e for the thiol

TABLE 1. Electronic Spectra of Mercapto Derivatives of Quinoline

CNDO, sp basis		CNDO, spd' basis		Assignment	Exptl.	
E, eV	f	E, eV	f		E, eV	f
8-Mercaptoquinoline (thiol form)[a]						
3,87	0,017	3,95	0,036	$\pi\rightarrow\pi^*$ (α)		
4,15	0,176	4,31	0,215	$\pi\rightarrow\pi^*$ (p)	3,74[5]	0,08
4,35	0,000	4,44	0,000	$n\rightarrow\pi^*$		
5,02	0,712	5,15	0,583	$\pi\rightarrow\pi^*$ (β)	5,06[5]	0,43
8-Mercaptoquinoline (mesoionic form)[b]						
1,86	0,038	1,63	0,033	$\pi\rightarrow\pi^*$ (p)	2.66[5] 2,08[c]	0,04
2,11	0,000	1,71	0,000	$n\rightarrow\pi^*$		
3,25	0,030	3,02	0,039	$\pi\rightarrow\pi^*$	3,88[5]	0,02
3,91	0,166	3,85	0,260	$\pi\rightarrow\pi^*$	4,46[5]	0,43
3,98	0,414	3,91	0,244	$\pi\rightarrow\pi^*$		
4,28	0,302	4,08	0,338	$\pi\rightarrow\pi^*$	4,95[5]	0,35
5,02	0,038	4,79	0,039	$\pi\rightarrow\pi^*$		
5,45	0,368	5,43	0,403	$\pi\rightarrow\pi^*$	5,90	0,60
5,66	0,210	5,60	0,165	$\pi\rightarrow\pi^*$		
5-Mercaptoquinoline (mesoionic form)[b]						
2,14	0,000			$n\rightarrow\pi^*$		
2,23	0,178			$\pi\rightarrow\pi^*$	2,65[9]	0,04
3,57	0,045			$\pi\rightarrow\pi^*$	3,85[9]	0,03
4,10	0,284			$\pi\rightarrow\pi^*$	4.46[9]	0,34
4,27	0,009			$\pi\rightarrow\pi^*$	4,88[9]	0,25
4,49	0,349			$\pi\rightarrow\pi^*$		
5-Mercapto-N-methylquinolinium ion						
2,18	0,000			$n\rightarrow\pi^*$		
2,26	0,181			$\pi\rightarrow\pi^*$ (p)	1.97[a] 2,64[b]	0,07 0,07
3,58	0,042			$\pi\rightarrow\pi^*$	3,26[c] 3,85[b]	0,03 0,04
4,12	0,292			$\pi\rightarrow\pi^*$	4,41[b]	0,34
4,30	0,007			$\pi\rightarrow\pi^*$	4.12[a]	0,18
4,49	0,324			$\pi\rightarrow\pi^*$	4,77[b]	0,26
5,18	0,006			$\pi\rightarrow\pi^*$		
5,63	0,230			$\pi\rightarrow\pi^*$	5,51[b]	0,30
5,70	0,210			$\pi\rightarrow\pi^*$		
6,17	0,060			$\pi\rightarrow\pi^*$	6,17[b]	0,63
6,42	0,754			$\pi\rightarrow\pi^*$		
8-Mercaptoquinoline (anionic form)[b]						
3,01	0,142			$\pi\rightarrow\pi^*$ (p)		
3,11	0,000			$n\rightarrow\pi^*$	3,38[5]	0,08
3,56	0,050			$\pi\rightarrow\pi^*$		
4,49	0,359			$\pi\rightarrow\pi^*$	4,77[5]	0,44
4,54	0,277			$\pi\rightarrow\pi^*$		
8-Mercaptoquinoline (cationic form)[b]						
3,36	0.116			$\pi\rightarrow\pi^*$ (p)	3,54[5]	0,04
3,87	0,200			$\pi\rightarrow\pi^*$ (α)	3,94[5]	0,08
4,63	0,445			$\pi\rightarrow\pi^*$ (β)	5,17[5]	0,42

a) Spectrum of a chloroform solution. b) Spectrum of an aqueous solution. c) Spectrum of a solution in bromobenzene.

and mesoionic forms, respectively. Consequently, within the framework of this model for these compounds the inclusion of the d orbitals of the sulfur atom in the AO basis does not introduce substantial qualitative and quantitative changes in the results of the calculations. In this case these orbitals play virtually no role in the formation of the chemical bond.

According to the material set forth above and the data in [4], the electronic structures and spectral properties of the mesoionic forms of 8-mercaptoquinoline and its oxygen-containing analog — 8-hydroxyquinoline — are extremely close. This is of interest in connection with the properties of the chelate compounds of these ligands. In [1] on the basis of the similarity in the absorption spectra of the mesoionic form and the 8-mercaptoquinoline complexes of transition metals (absorption at 500-600 nm in the case of Pt, Pd, Ni, etc.) it is assumed that the ligands in the complexes have mesoionic structures.

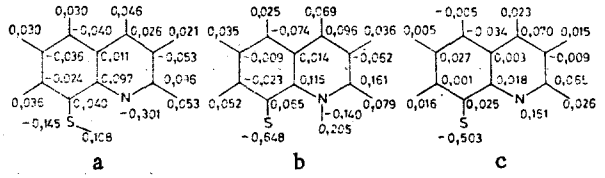

Fig. 1. Electron-density distribution in the 8-mercaptoquinoline molecule: a) thiol form; b) mesoionic form; c) diagram of the change in the charge on the atoms on passing from the thiol form to the mesoionic form.

The long-wave band in the spectra of the corresponding 8-hydroxyquinoline complexes of transition metals is shifted substantially to the short-wave region (~400 nm [1]). If one follows the hypothesis in [1], the ligands in these chelate compounds do not have the structure of the mesoionic form. It is known that the corresponding band in the spectrum of the meosionic form of the 8-hydroxy-N-methylquinolinium ion is found at 600 nm [4].

The negative charge in the mesoionic form of 8-mercaptoquinoline is localized on the p_σ orbitals of the sulfur atom. However, this orbital participates in the formation of the M—S bond in the 8-mercaptoquinoline complexes of transition metals. Thus in these chelate compounds, the central atom of which forms strong M—S and M—N bonds (for example, with Pd and Pt [6]) the mesoionic structure of the ligands and, correspondingly, the presence of a negative charge on the sulfur atom can be due only to the population of the d orbitals of the sulfur atom.

M—O and M—N bonds are also formed in the 8-hydroxyquinoline complexes of transition metals [7]. However, the absence of energically favorable vacant orbitals excludes the possibility of a mesoionic structure for the ligands, as in the case of 8-mercaptoquinoline complexes. The ligands in 8-hydroquinoline complexes of transition metals, which form M—O and M—N bonds, possibly have a structure similar to the structure of the cationic form (absorption at ~400 nm [1]).

Diagrams of the electron-density distribution in the thiol and mesoionic forms of 8-mercaptoquinoline are presented in Fig. 1. A diagram of the differential electron density, which reflects the change in the electronic structure on passing from the thiol form to the mesoionic form, is also presented.

As in the case of the cationic form, protonation of the nitrogen atom in the mesoionic form gives rise to strong polarization of the σ framework of the molecule. The highest electron density is localized on the sulfur atom (—0.765 e), and the lowest is localized on the nitrogen atom (+0.494 e). The positive charge of the σ framework on the nitrogen atom is partially compensated by polarization of the electrons along the π orbitals. As a result of this, the negative charge on the sulfur atom and the positive charge on the nitrogen atom and the "2" and "4" carbon atoms of the quinoline ring increase considerably during the development of the mesoionic form (Fig. 1c). The increase in the negative charge on the sulfur atom and the positive charge on the nitrogen atom in the mesoionic form is in good agreement with the data from the x-ray electron spectra [8].

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