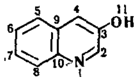
ELECTRONIC STRUCTURE AND REACTIVITY OF 3-HYDROXYQUINOLINE

B. E. Zaitsev, N. A. Andronova,
V. T. Grachev, V. P. Lezina,
K. M. Dyumaev, and L. D. Smirnov

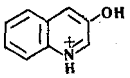
UDC 547.831.7:541.67

The reactivity indexes of the neutral, dipolar, cationic, and anionic forms of 3-hydroxyquinoline were calculated by the simple MO LCAO method using dynamic and statistical approximations. The predicted (on the basis of the localization energies) charge distributions, boundary densities, free valence indexes, and orientations of electrophilic substituents for the cationic and anionic forms of 3-hydroxyquinoline are in good agreement with the experimental data. The orientations of nucleophilic and radical substituents for the four forms of 3-hydroxyquinoline are predicted. The reactivity indexes of the neutral form of 3-hydroxyquinoline were calculated by means of the Pariser–Parr–Pople method.

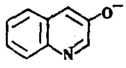
In our plan for investigating the relationship between the electronic structure and chemical behavior in substitution reactions in a number of hydroxy derivatives of heterocyclic compounds, we turned to a quantum-mechanical calculation of the structure of 3-hydroxyquinoline. The goal of the present study was to obtain the reactivity indexes using approximations of isolated and reacting forms of the molecules and correlation of them with the experimental data.



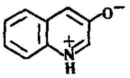
A



B



C



D

The calculation of the possible forms (A, B, C, and D) of 3-hydroxyquinoline [1, 2] was performed with the simple Hückel MO LCAO method with a BÉSM-4 computer. The coulombic integrals (Table 1) were found by variation, and the resonance integrals were taken from Pullman. The Hückel MO program was kindly placed at our disposal by D. A. Bochvar and A. Tutkevich. The neutral molecule was calculated by the Pariser–Parr–Pople (PPP) method with the program of D. I. Kagan [3].

TABLE 1. Calculated Parameters

Element	Form	Coulombic integral, $\alpha_2 = \alpha_0 + h_2\beta_0$	Form	Coulombic integral, $\alpha_2 = \alpha_0 + h_2\beta_0$
Carbon	A	$h_{C_2, C_3, C_{10}} = 0$	C	$h_{C_2, C_3, C_{10}} = 0$
Nitrogen		$h_N = 0{,}2$		$h_N = 0{,}2$
Oxygen		$h_O = 2{,}0$		$h_O = 1{,}2$
Carbon	B	$h_{C_2, C_3, C_{10}} = 0$	D	$h_{C_2, C_3, C_{10}} = 0$
Nitrogen		$h_N = 0{,}34$		$h_N = 0{,}34$
Oxygen		$h_O = 2{,}0$		$h_O = 1{,}2$

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Scientific-Research Institute of Organic Intermediates and Dyes, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 191-196, February, 1972. Original article submitted September 24, 1970.

TABLE 2. Energy Characteristics of 3-Hydroxyquinoline in Beta Units

Compound form	DE_π	DE_π/n	E_{HOMO}	E_{LFMO}	ΔE ($E_{HOMO}-E_{LFMO}$)	λ_{max}, nm
A	3,81	0,3175	0,6284	0,5911	1,2195	320
B	3,80	0,3166	0,6505	0,5650	1,2155	340
C	3,82	0,3183	0,6007	0,5927	1,1934	350
D	3,87	0,3225	0,5951	0,5703	1,1654	367

TABLE 3. Bond Orders, Bond Lengths, and π-Electron Densities

Form	Bond	Bond order	Calculated bond length, Å	Atom	π-Electron density
A	1—2	(0,7544)* 0,7244	1,319	1	1,0852
	1—10	(0,5142) 0,5513	1,350	2	0,9741
	2—3	(0,5104) 0,5906	1,409	3	0,9721
	3—4	(0,7256) 0,7100	1,389	4	1,0094
	4—9	(0,5241) 0,5569	1,413	5	1,0015
	9—5	(0,5306) 0,5540	1,415	6	1,0012
	9—10	(0,5579) 0,5174	1,422	7	0,9999
	5—6	(0,7551) 0,7245	1,386	8	1,0041
	6—7	(0,5678) 0,6033	1,407	9	0,9996
	7—8	(0,7551) 0,7237	1,386	10	0,9913
	8—10	(0,5289) 0,5561	1,415	11	1,9610
	3—11	(0,3434) 0,1981	1,388		
B	1—2	0,7186	1,320	1	1,1458
	1—10	0,5476	1,350	2	0,9448
	2—3	0,5918	1,409	3	0,9745
	3—4	0,7094	1,389	4	0,9903
	4—9	0,5565	1,415	5	0,9983
	9—5	0,5541	1,415	6	1,0021
	9—10	0,5179	1,422	7	0,9954
	5—6	0,7243	1,386	8	1,0077
	6—7	0,6035	1,407	9	1,0001
	7—8	0,7232	1,386	10	0,9793
	8—10	0,5572	1,414	11	1,9611
	3—11	0,1974	1,388		
C	1—2	0,7261	1,319	1	1,0848
	1—10	0,5502	1,350	2	0,9757
	2—3	0,5857	1,410	3	0,9760
	3—4	0,7040	1,390	4	1,0168
	4—9	0,5583	1,415	5	1,0033
	9—5	0,5536	1,415	6	1,0012
	9—10	0,5168	1,422	7	1,0017
	5—6	0,7244	1,386	8	1,0039
	6—7	0,6033	1,407	9	0,9996
	7—8	0,7232	1,386	10	0,9935
	8—10	0,5568	1,415	11	1,9430
	3—11	0,2371	1,380		
D	1—2	0,7221	1,320	1	1,1442
	1—10	0,5457	1,351	2	0,9523
	2—3	0,5798	1,411	3	0,9690
	3—4	0,6959	1,391	4	1,0138
	4—9	0,5594	1,414	5	1,0029
	9—5	0,5532	1,415	6	1,0021
	9—10	0,5166	1,422	7	1,0002
	5—6	0,7243	1,386	8	1,0070
	6—7	0,6035	1,407	9	0,9998
	7—8	0,7224	1,386	10	0,9855
	8—10	0,5584	1,414	11	1,9227
	3—11	0,2770	1,372		

---

*The values calculated by the PPP method are given in parentheses.

TABLE 4. Reactivity Indexes of 3-Hydroxyquinoline

Form	Atom No.	L_E	L_N	L_R	Q	f_E	f_N	F_i
A	2	2,5510	2,4500	2,5060	(+0,0899)* +0,0259	(0,0259) 0,0233	(0,3542) 0,1069	(0,4672) 0,417
	4	2,2612	2,2580	2,2596	(−0,0378) −0,0094	(0,3424) 0,1906	(0,3623) 0,1849	(0,4823) 0,4651
	5	2,3540	2,3522	2,3536	(−0,0077) −0,0015	(0,3225) 0,1911	(0,2857) 0,1651	(0,4464) 0,4535
	6	2,7506	2,7506	2,7506	(−0,0034) −0,0012	(0,0187) 0,0540	(0,1471) 0,0656	(0,4022) 0,4042
	7	2,4732	2,4722	2,4727	(−0,0017) +0,0001	(0,2777) 0,0809	(0,1050) 0,0649	(0,4091) 0,405
	8	2,3004	2,3004	2,3004	(+0,0022) −0,0041	(0,2467) 0,1777	(0,3004) 0.1659	(0,4480) 0,4522
B	2	2,5762	2,3040	2,4401	+0,0552	0,0144	0,1233	0,4216
	4	2,3064	2,2140	2,2602	+0,0097	0,1773	0,1992	0,4661
	5	2,3054	2,2814	2,2934	+0,0017	0,1989	0,1566	0,4536
	6	2,4802	2,4802	2,4802	−0,0021	0,0616	0,0591	0,4042
	7	2,4886	2,4556	2,4721	+0,0046	0,0807	0,0667	0,4053
	8	2,3018	2,3018	2,3018	−0,0077	0,1880	0,1515	0,4516
C	2	2,4930	2,3612	2,4321	+0,0243	0,0064	0,1097	0,4202
	4	2,144	2,1616	2,1880	−0,0168	0,2062	0,1819	0,4697
	5	2,2830	2,2688	2,2759	−0,0033	0,1727	0,1642	0,4540
	6	2,4800	2,4800	2,4800	−0,0012	0,0400	0,0665	0,4043
	7	2,4592	2,4400	2,4496	−0,0017	0,0868	0,0637	0,4055
	8	2,3008	2,3008	2,3008	−0,0039	0,1429	0,1659	0,4520
D	2	2,5088	2,2932	2,4010	+0,477	0,000061	0,1335	0,4301
	4	2,2008	2,1726	2,1926	−0,0138	0,2070	0,1857	0,4763
	5	2,2822	2,2744	2,2783	−0,0029	0,1622	0,1543	0,4545
	6	2,4802	2,4802	2,4802	−0,0021	0,0289	0,0617	0,4042
	7	2,4578	2,4470	2,4524	−0,0002	0,0909	0,0631	0,4061
	8	2,3030	2,3030	2,3030	−0,0070	0,1222	0,1534	0,4512

*The RI values calculated by the PPP method are presented in parentheses.

TABLE 5. Predicted (on the basis of localization energies) and Experimental Orientations of Electrophilic Substituents in 3-Hydroxyquinoline

Molecule	Hückel MO method	Exptl. data
A	4>8>5>7>2>6	—
B	4⩾5=8>7, 6>2	4 (NO_2^+, Br^+)
C	4>5>8>7>6>2	4 (Br^+, Cl^+, I^+, ArN_2^+, R_2N)
D	4>5>8>7>6>2	

The calculation of the energy levels of the A, B, C, and D forms demonstrates that the π electrons of the rings and the unshared pair of electrons of the exocyclic oxygen atom are located in bonding orbitals, which is responsible for the formation of a stable, closed molecular shell.

To estimate the thermodynamic stability of the A, B, C, and D forms, we calculated the energies of the π-electron delocalization energies (DE_π) and the energies of delocalization per π electron (DE_π/n). It is apparent from Table 2, that these values are close to those in benzene (0.333 β).

The existence of forms A and D of 3-hydroxyquinoline in equilibrium should be associated with the proximity of the energies of these forms, particularly DE_π. The calculated DE_π and DE_π/n values range from 3.80 to 3.87 and 0.3166 to 0.3225, respectively. The delocalization energies of the forms that contain an exocyclic anionic oxygen are somewhat higher than the DE_π values of the hydroxyl-containing forms. The data obtained on DE_π are evidence in favor of dipolar and anionic forms of 3-hydroxyquinoline. However, if one takes into account the energy of the σ bonds of the OH groups (101.36 ± 0.3 kcal/mole) and of the NH groups (83 ± 3 kcal/mole) [4], one should expect that the neutral form (A) is to be preferred over the dipolar or anionic form in an inert medium. In fact, investigations of the UV spectra attest to the absence of the dipolar form for 3-hydroxyquinoline. The order (p_{C-O}) and length of the C–O bond and the π-electron charge (Q_i) on the oxygen atom (Table 3) are evidence for interaction of the exocyclic oxygen atom with the pyridine ring in 3-hydroxyquinoline. In this case, the conjugation of the anionic oxygen atom is considerably higher than that of the hydroxyl oxygen: 1) the p_{C-O} bond order is 20-40% higher than the

p_{C-OH} bond order; 2) the bond lengths found from the calculated p_{xy} values in the neutral form are 1.388 Å compared with 1.372-1.380 Å in the anionic form; 3) the π-electron charge on the anionic oxygen atom is almost twice that (Q_{π}) on the phenolic oxygen atom.

The interaction of the exocyclic oxygen atom with the aromatic ring is in agreement with the x-ray diffraction data, according to which the interatomic C−O distance [5] in the model compound − 8-hydroxyquinoline − is reduced by 0.15 Å as compared with C−O in saturated compounds. The calculated bond orders and lengths of the quinoline ring are high (Table 3), which may be associated with the high degree of aromatic character of the ring. However, in contrast to 3-hydroxypyridine, a considerably greater difference in the bond orders in the rings is observed in the studied compounds. Thus, the orders of the 1−2, 3−4, 5−6, and 7−8 bonds are considerably higher than the orders of the remaining bonds in the ring. This confirms the hypothesis of fixation of the double bonds of the quinoline ring, which is responsible for its chemical behavior [6]. A similar fixation of the double bonds was previously observed [7] for β-naphthol.

The interatomic distances for the four forms of 3-hydroxyquinoline (Table 3), calculated from formula [8] using the bond orders that we obtained, are in good agreement with the known experimental data on the interatomic distances of the $C \overset{\cdot}{=} C$ and $C \overset{\cdot}{=} N$ bonds in 8-hydroxyquinoline [5].

The distribution of the π-electron density in the 3-hydroxyquinoline ring is not uniform (Table 3). This is due to the high electronegativity of the cyclic nitrogen atom (3.0) as compared with the electronegativity of the carbon atom (~ 2.5). In this case, the negative π-electron charge is concentrated on the nitrogen atom. Protonation of the nitrogen atom leads to a pronounced increase in the negative π-electron charge on nitrogen and to a corresponding decrease in the charge on the carbon atom.

The differences between the higher occupied molecular orbital (HOMO) and the lower free molecular orbital (LFMO) correlate satisfactorily with the wavelength of the absorption maximum in the electronic spectrum of the corresponding form (Table 2).

The π-electron characteristics [reactivity indexes (RI)] of the ground state of the molecule were used to examine the reactivities of the molecules in the static state (π complex intermediate state), while the localization energies were calculated for examination of the reactivities in the dynamic approximation (with a σ complex as the intermediate state). The latter usually better describes aromatic substitution than do the RI of molecules in the static state [9].

The experimental data demonstrate that the most reactive position of the pyridine ring in nitration and bromination in acidic media is the 4 position. The calculated localization energies (L_E) are in good agreement with the above-indicated experimental data. Thus the localization energies in the 4, 8, and 5 positions are practically identical, while the localization energy for the 2 position is very high. There are probably additional conditions associated with the specificity of the electrophilic agents that are responsible for reaction primarily at the 4 position.

3-Hydroxyquinoline is in the anionic form (C) in reactions that occur in alkaline media [10, 11] (azo coupling, aminomethylation, iodination, and bromination). The calculation of L_E for the anionic form of 3-hydroxyquinoline indicates maximum reactivity at the 4 position and minimum reactivity at the 2 position of the pyridine ring. The latter is in agreement with the available experimental data, according to which 4-substituted reaction products are formed during aminomethylation and iodination of 3-hydroxyquinoline. In contrast to the cationic form, the condensed benzene ring is comparatively less reactive than the 4 position of the pyridine ring according to the calculated L_E in the anionic form (Tables 4 and 5).

There are no data available for nucleophilic and radical substitution reactions. The predicted order of substitution for these reactions according to the calculated L_N and L_R values is presented in Tables 4 and 5.

It is of interest to examine the orientation of aromatic substitution proceeding from the reactivity indexes of the static 3-hydroxyquinoline model. For the neutral and dipolar forms, the predicted orders of orientation of electrophilic, nucleophilic, and radical substitutions with respect to the charge distribution (Q), boundary electron densities (f_E, f_N), and the free valence indexes (F_i) are in complete agreement with the orders of orientations obtained on the basis of the localization energies (Tables 4 and 5). It should be noted that the RI of form A in the static approximation (Table 4), which were obtained by the PPP method, are in good agreement with the RI obtained by the Hückel MO method.

An examination of the RI (Q, f_E, f_N, F_i) of the anionic form (C) gives the same order of aromatic substitution as the calculated values of the localization energies (L_E, L_N, L_R). Thus the RI (L_E, Q, f_E, F_i) predict an order of orientation of electrophilic substituents that is in agreement with the experimental data.

The calculated Q and f_E values for the cationic form predict that the condensed benzene ring is the most reactive center.

LITERATURE CITED

1. A Bryson, J. Am. Chem. Soc., 82, 4871 (1960).
2. F. S. Mason, J. Chem. Soc., 5010 (1957); 674 (1958).
3. Yu. A. Kruglyak, G. G. Dyadyusha, V. A. Kuprievich, L. M. Podol'skaya, and G. I. Kagan, Methods for the Calculation of Electronic Structures and Electronic Spectra [in Russian], Kiev (1969), p. 108.
4. V. I. Vedeneev, L. V. Gurvich, V. N. Kondrat'ev, V. A. Medvedev, and E. L. Frankevich, Energies Required to Break Chemical Bonds. Ionization Potentials and Electron Affinities [in Russian], Izd. Akad. Nauk SSSR, Moscow (1962), p. 81.
5. P. Murray-Rust and J. D. Wright, J. Chem. Soc., A, 247 (1968).
6. G. P. Bean, A. R. Katritzky, and A. Marzee, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 16 (1968).
7. N. Donaldson, Chemistry and Technology of Compounds of the Naphthalene Series [Russian translation], Moscow (1953), p. 18.
8. M. J. S. Dewar and T. Morita, J. Am. Chem. Soc., 91, 4796 (1969).
9. A. Streitwieser, Molecular Orbital Theory for Organic Chemists, Wiley (1961).
10. L. D. Smirnov, N. A. Andronova, V. P. Lezina, and K. M. Dyumaev, Izv. Akad. Nauk SSSR, Ser. Khim., 2382 (1970).
11. M. Shimizi, J. Pharm. Soc. Japan, 64, 10a, 47 (1944).