

344. *Some 8-Hydroxyquinolines and their Nickel(II) Chelates. Part I. Hückel LCAO Calculations for 8-Hydroxyquinolines.*

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Hückel LCAO calculations are described for 8-hydroxyquinoline, and its chemistry is briefly discussed in the light of the resulting charge distribution and localisation energies. The calculations are extended to deal with 5- and 7-halogeno- and 5,7-dihalogeno-derivatives.

THE analytical use of 8-hydroxyquinoline and its derivatives has been the subject of a considerable number of papers since Hahn¹ and Berg² first established its potential as a precipitant for metal ions. The present work arose out of a desire to correlate the properties of the metal complexes with their structures. The reagents studied were 8-hydroxyquinoline and its 5- and 7-halogeno- and 5,7-dihalogeno-derivatives.

It is well known that 8-hydroxyquinoline and its derivatives form chelate complexes with metal ions.³ Although similar in many respects, the nickel(II) complexes differ in some of their properties, *e.g.*, magnetic susceptibilities and spectra. For example, the parent compound, bis-(8-hydroxyquinolinato)nickel(II), is paramagnetic with a moment of 3.2 Bohr magnetons, whilst the corresponding chelates with the derivatives are, with one exception, diamagnetic.⁴ We thought that this difference might be explained by an analysis of the charge distribution in the reagents, and Hückel LCAO calculations were carried out.

Unsubstituted 8-Hydroxyquinoline.—Application of the usual variation method,⁵ leads to the well known secular determinant $|H_{ij} - S_{ij}E| = 0$, where H_{ij} is the bond integral and S_{ij} the overlap integral for the orbitals ϕ_i and ϕ_j , and H_{ii} denotes the Coulomb term of ϕ_i . The ϕ 's are the p orbitals which take part in the molecular orbitals. This determinant can be simplified by making the usual approximations of neglecting the overlap integrals and also bond integrals between non-neighbouring atoms. Further simplification can be achieved by taking the Coulomb terms of all the carbon-based p orbitals to be equal, and similarly for the carbon-carbon bond integrals. In considering the heteroatoms, it is necessary to take into account the fact the Coulomb terms of the Np_π and Op_π orbitals differ from those of the Cp orbitals, and also that the bond integrals for the bonds $Np_\pi-Cp_\pi$ and $Op_\pi-Cp_\pi$ differ from those of the bonds $Cp_\pi-Cp_\pi$. These differences can be expressed in the following form:

$$\begin{aligned} H(Np_\pi, Np_\pi) &= H_{CC} + m\beta_{CC} & H(Np_\pi, Cp_\pi) &= x\beta_{CC} \\ H(Op_\pi, Op_\pi) &= H_{CC} + n\beta_{CC} & H(Op_\pi, Cp_\pi) &= y\beta_{CC} \end{aligned}$$

where H_{CC} and β_{CC} denote, respectively, the Coulomb term and bond integral for the Cp_π orbitals, and m , n , x , and y are parameters. The immediate problem is to assign reasonable values to these parameters.

In a treatment of quinoline, Brown and Harcourt,⁶ chose the value $H(Np_\pi, Cp_\pi) = 1.0 \beta_{CC}$, as a result of detailed calculations. They also showed the resultant charge distribution to be insensitive to small variations in this parameter. It is not unreasonable to assume a similar result to be true for 8-hydroxyquinoline. They also made the following assignments for the nitrogen Coulomb term parameter: N(core charge +1) $m = 0.5$, and N(core charge +2) $m = 2.0$, where the first value is to be used in calculations on the neutral

¹ Hahn *Z. Angew. Chem.* 1926, **39**, 1198.

² Berg, *J. prakt. Chem.*, 1927, **115**, 178.

³ Hollingshead, "Oxine and its Derivatives," Butterworths, London, 1954.

⁴ Burton and Davis, unpublished work.

⁵ Daudel, Lefebvre, and Moser, "Quantum Chemistry," Interscience, New York and London, 1959, p. 137.

⁶ Brown and Harcourt, *J.*, 1959, 3451.

molecule and the second for the protonated species. These values are taken over into the present work.

Relatively little work has been done on phenols. In estimating the bond integral parameter for the carbon-oxygen bond we made use of the relation due to Lennard-Jones,⁷ which gives this parameter as the ratio between experimentally obtainable bond energies, *i.e.*, we put,

$$y = [E(\text{C}=\text{O}) - E(\text{C}-\text{O})]/[E(\text{C}=\text{C}) - E(\text{C}-\text{C})]$$

where $E(\text{C}=\text{O})$ represents the bond energy of the carbon-oxygen double bond, and the other terms have the corresponding meanings. However, as pointed out by Pilar,⁸ it is more reasonable to take $E(\text{C}=\text{O})$ as the bond energy of the carbon-oxygen bond in the compound concerned, rather than the bond energy in, say, acetone. Estimation of the bond length,⁹ and interpolation in the bond-energy-bond-length relationship due to Glockler,¹⁰ yielded a value of ~ 0.3 for y . Support for this comes from the work of Igea Lopez-Vazquez,¹¹ who takes the value to be 0.27. A reasonable value¹² for the Coulomb term parameter for oxygen appears to be 1.1. A value of 1.2 has been quoted by Matsen.¹³ However, as we considered the data for oxygen to be not as reliable as those for nitrogen, we carried out a variation of both n and y until a good fit was obtained for both the first $\pi-\pi^*$ transition energy and the carbon-oxygen bond order. The latter is estimated by noting the bond length⁹ and interpolating in the bond-length-bond-order relation due to Pilar.⁸ In this manner we find that $n = 1.5$ with $y = 0.8$ for the neutral molecule and $n = 0.75$ with $y = 0.8$ for the anion. The failure of the Lennard-Jones relation may well arise because of difference of electronegativity of the atoms concerned.

The first $\pi-\pi^*$ transition energy is calculated from the equation

$$\nu \text{ (cm.}^{-1}\text{)} = 19,020\delta + 10,520$$

where δ is the LCAO calculated energy difference between the bonding and antibonding orbitals concerned.¹⁴ This correlation is derived through an analysis of the spectra of 43 aromatic benzenoid hydrocarbons, and we make the assumption that it is valid also for the heteroaromatic compounds discussed here. The charge distributions are presented graphically in Fig. 1, and localisation energies in Table I.

TABLE I.

(a) Electrophilic localisation energies, (b) nucleophilic localisation energies, and (c) radical localisation energies, for 8-hydroxyquinoline.

In all cases, $x = 1.0$, $y = 0.8$. For the "acid" values $m = 2.0$, $n = 1.5$; for the "neutral" values $m = 0.5$, $n = 1.5$; and for the "alkaline" values $m = 0.5$, $n = 0.5$. All energies are given in units of $-\beta_{cc}$.

Position	(a)			(b)			(c)		
	Acid	Neut.	Alk.*	Acid	Neut.	Alk.*	Acid	Neut.	Alk.*
2	2.812	2.622	2.406	1.712	2.264	2.292	2.262	2.443	2.349
3	2.528	2.486	2.490	2.528	2.486	2.490	2.528	2.486	2.490
4	2.796	2.422	2.270	1.800	2.154	2.178	2.298	2.288	2.224
5	2.238	2.164	1.944	2.198	2.358	2.438	2.218	2.261	2.191
6	2.502	2.490	2.504	2.502	2.490	2.504	2.502	2.490	2.504
7	2.352	2.268	1.988	2.304	2.524	2.586	2.328	2.396	2.287

* These values have been calculated using $n = 0.5$; the recommended value for the oxygen Coulomb parameter is $n = 0.75$.

⁷ Lennard-Jones, *Proc. Roy. Soc.*, 1931, **A158**, 280.

⁸ Pilar, *J. Mol. Spectroscopy*, 1960, **5**, 72.

⁹ *Chem. Soc. Special Publ.*, No. 11, p. S17.

¹⁰ Glockler, *J. Phys. Chem.*, 1958, **62**, 1049.

¹¹ Igea Lopez-Vazquez, *Anales real Soc. españ. Fis. Quim.*, 1955, **51**, B, 203.

¹² Ref. 5, pp. 74, 75.

¹³ Matsen, *J. Amer. Chem. Soc.*, 1950, **72**, 5243.

¹⁴ Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, 1961, p. 217.

Substituted 8-Hydroxyquinolines.—The substituted 8-hydroxyquinolines considered here are the 5- and 7-halogeno- and 5,7-dihalogeno-compounds. In introducing an additional atom, X, into the π system at least three new parameters must be introduced; these involve the Coulomb term for the Xp_π orbital, the bond integral for the bond $Xp_\pi-Cp_\pi$, and an auxiliary inductive parameter which allows for a change in the Coulomb term of the Cp_π orbital on the atom to which the halogen is attached. This last effect becomes significant when atoms of widely different electronegativities are joined. The new parameters can be expressed in the following form:

$$H(Xp_\pi, Xp_\pi) = H_{CC} + h\beta \quad H(Xp_\pi, Cp_\pi) = z\beta_{CC} \quad H(Cp_\pi, Cp_\pi) = H_{CC} + h'\beta_{CC}$$

Following some work of Robertson and Matsen,¹⁵ we set $h' = 0.1h$ if the carbon atom concerned is bonded to halogen, and equal to zero if it is not. It remains to estimate h and z .

A value of z , for $X = \text{Cl}$, has been estimated as ~ 0.33 from measurements of the asymmetry of the chlorine nuclear electric quadrupole interaction.¹⁶ A value of 0.56 has been assigned from a study of valence states and ionisation potentials.^{17,18} On the basis

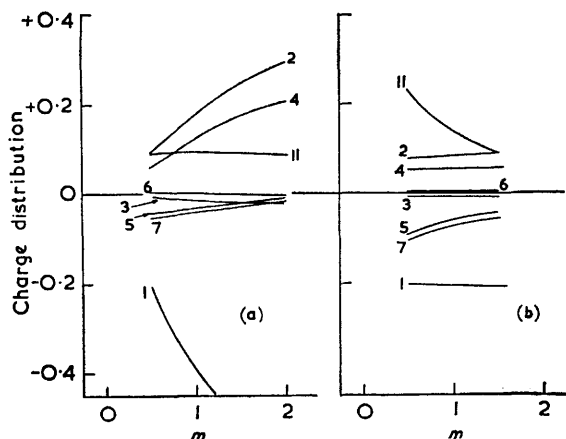


FIG. 1. (a) Variation of charge distribution with nitrogen Coulomb terms. Oxygen Coulomb term parameter $n = 1.5$. (b) Variation of charge distribution with oxygen Coulomb term. Nitrogen Coulomb term parameter $m = 0.5$.

of overlap integrals, a value of 0.6 has been suggested.¹⁹ The value chosen for the present work is 0.4 .²⁰ For $X = \text{Br}$, z has been estimated as ~ 0.4 in a treatment of vinyl bromide which included overlap.²¹ The value is probably less than that for chlorine, and a value of 0.3 is selected for the present work. This value can also be assigned to the $Ip_\pi-Cp_\pi$ bond integral.²⁰

Using the selected value of z , the energy levels of the particular halogen compound are calculated for a range of values of the Coulomb term parameter h . Fig. 2 shows the energy levels of 5-chloro-8-hydroxyquinoline as a function of the chlorine Coulomb term parameter. The dimensionless quantity $(E - E')/E$ is then calculated as a function of h , where E is the LCAO calculated energy of the first $\pi-\pi^*$ transition for the present compound, and E' is the corresponding energy for the derivative. This is compared with the experimentally obtained $(\nu - \nu')/\nu$, where ν is the spectral frequency at which the first $\pi-\pi^*$ transition of the parent occurs, and ν' the corresponding frequency for the derivative. That value of h is selected for which the two expressions are equal (see Fig. 3). The values of h so derived are: $h(\text{Cl}) = 0.9$, and $h(\text{Br}) = 0.7$. The iodo-compounds are not considered.

¹⁵ Robertson and Matsen, *J. Amer. Chem. Soc.*, 1950, **72**, 5252.

¹⁶ Bersohn, *J. Chem. Phys.*, 1954, **22**, 2078.

¹⁷ Goldstein, *J. Chem. Phys.*, 1956, **24**, 507.

¹⁸ Howe and Goldstein, *J. Chem. Phys.*, 1957, **26**, 7.

¹⁹ Simonetta *et al.*, *Mol. Phys.*, 1958, **1**, 181.

²⁰ Ref. 14, p. 126.

²¹ Howe and Goldstein, *J. Chem. Phys.*, 1957, **27**, 831.

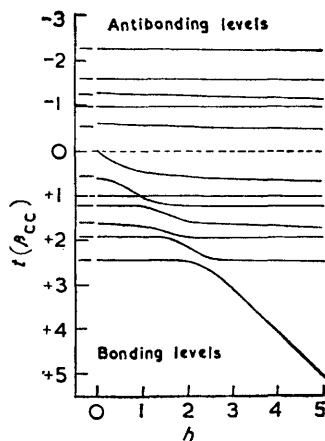


FIG. 2. Energy levels of 5-chloro-8-hydroxyquinoline as a function of the chlorine Coulomb term parameter. Energies of levels are expressed as $H_{cc} + t\beta_{cc}$. Unperturbed levels are shown on the left.

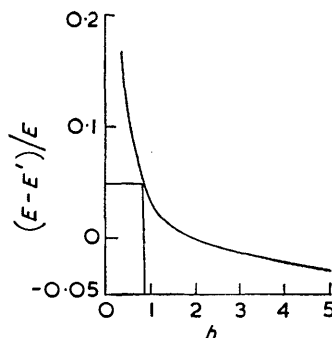
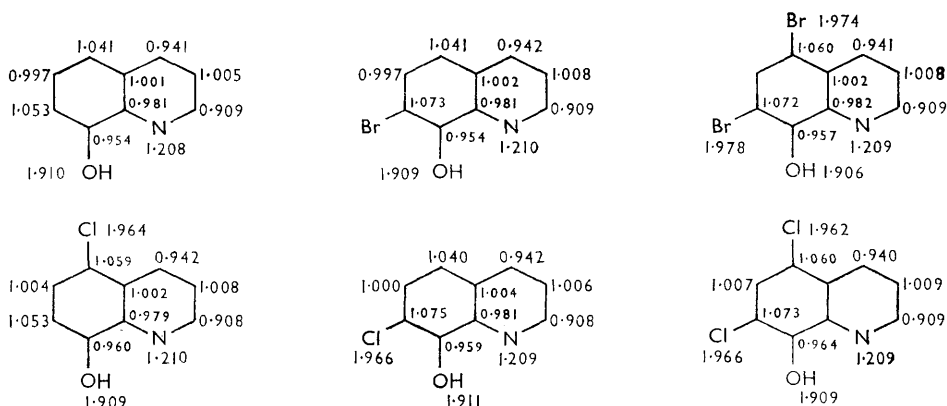


FIG. 3. Variation of the relative energy shift $(E - E')/E$ with the chlorine Coulomb term parameter. Experimental value of $(\nu - \nu')/\nu = +0.054$; $h = 0.90$.

In dealing with the dichloro- and dibromo-derivatives, it is assumed that the two halogen atoms are equivalent and could, therefore, be represented by the same parameters.



Charge distributions calculated for the selected values of the parameters are shown on the formulæ, and the frequencies of the first $\pi-\pi^*$ transitions and the derived values of the Coulomb term parameter are shown in Table 2.

TABLE 2.

Frequencies of the first $\pi-\pi^*$ transitions and the derived values of the Coulomb term parameter for substituted 8-hydroxyquinolines.

Substituents	λ (m μ)	ν (cm. ⁻¹)	h	Substituents	λ (m μ)	ν (cm. ⁻¹)	h
Unsubst.	315	31,750	—	5,7-Dichloro- ...	329	30,395	1.00
5-Chloro-	333	30,030	0.85	7-Bromo-	333	30,030	0.60
7-Chloro-	332	30,120	0.75	5,7-Dibromo- ...	330	30,300	0.75

DISCUSSION

The chemistry of 8-hydroxyquinoline has been reviewed by Phillips.²² Concerning the phenol-like reactions, we note the presence of significant net negative charge at positions

²² Phillips, *Chem. Rev.*, 1956, **56**, 271.

1770 *Some 8-Hydroxyquinolines and their Nickel(II) Chelates. Part I.*

5 (0.041) and 7 (0.053). These positions also have relatively low electrophilic localisation energies. This accords well with the experimental observation that positions 5 and 7 are the centres for electrophilic attack. The two positions have approximately the same net charges and localisation energies. The charge distributions given show that, within the approximation of the model, a halogen substituent does not markedly alter the π charges at other positions in the ring. We consider this to be an explanation of the fact that in halogenation with an equimolar ratio of reactants a mixture of mono- and di-substituted products is obtained, whilst with a 2 : 1 molar ratio the dihalogenated product is almost exclusively formed.

With regard to nucleophilic attack the position is less satisfactory. On the bases of charge distribution and nucleophilic localisation energy, it appears reasonable to suppose that positions 2 and 4 should both undergo nucleophilic attack. Only 2-substitution has been recorded in the literature. This seems rather anomalous since quinoline itself is reactive at these positions and there appears to be no great difference between the two compounds. In the case of amination an explanation may lie in the following. The order of reactivity of the quinoline positions towards the amide ion, NH_2^- (presumably the aminating species), is unambiguously $2 > 4 > \text{others}$.²³ The net charges for quinoline⁶ at the 2- (+0.10) and the 4-position (+0.07) are greater than those for 8-hydroxyquinoline (+0.09 and +0.06, respectively), for the neutral molecule with the same values for the nitrogen parameters, and ignoring any auxiliary inductive parameters. The placing of 8-hydroxyquinoline in strongly basic media will cause ionisation of the hydroxyl function with a consequent reduction in the net positive charges at the 2- and the 4-position to +0.08 and +0.05, respectively. Although the charge differences are not very large, they may be sufficient to account for the decrease in reactivity of the two positions in going from quinoline to 8-hydroxyquinoline. A further complicating factor is that the anion can chelate with metal ions in the system, *e.g.*, if $\text{Ba}(\text{NH}_2)_2$ is the source of amide ion, with consequent change in the charge distribution. It is known that the Ba^{2+} ion exerts an effect on the amination of quinoline,⁶ which should be more apparent with the 8-hydroxyquinoline anion because of its strong chelating properties. As a suggestion of how chelation can change the charge distribution, the π -LCAO calculation for bis-(8-hydroxyquinolinato)-nickel(II) indicates that the net π charges at positions 2 and 4 are, respectively, +0.05 and +0.02. An effect such as this may be sufficient to account for the apparently complete inhibition of the 4-position.

It is of the greatest importance to carry out a variation of parameters in discussing heteroaromatic systems. Protonation of the nitrogen function and dissociation of the hydroxyl function both lead to large changes in the parameters with consequent changes in the charge distributions. A full variation of the critical parameters should enable one to construct a good dynamic picture of the reactivity of the hetero-system. This is merely a reflection of chemical experience that the course of a reaction can be controlled by controlling the conditions.

The charges at the oxygen and nitrogen functions do not differ markedly in different compounds. However, these charges must differ, in view of the different acid dissociation constants of the parent and its derivatives. Wheland²⁴ experienced a similar difficulty in attempting to account for the different reactivities of halogenobenzenes by means of a static-charge distribution model. By the choice of special values of the parameters their chemistry can be "explained." The halogen parameters derived from spectra do not completely account for the chemistry of the compounds because they are derived by considering the energy difference between two orbitals, whereas the charges depend, for the 8-hydroxyquinolines, upon perhaps seven or eight orbitals. Only a general picture

²³ Bergstrom, *J. Amer. Chem. Soc.*, 1934, **56**, 1748; *J. Org. Chem.*, 1938, **2**, 411.

²⁴ Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

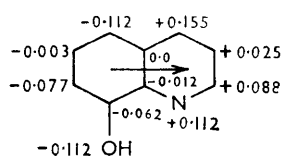
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1771

of the chemical reactivity of these compounds can, therefore, be expected to result from such a naïve analysis.

From a knowledge of the LCAO orbital coefficients, the charge distribution in the parent molecule, before and after the first π - π^* transition, can be calculated. The resultant changes in the charges at the various positions are shown. It can be seen that the transition



involves a movement of electronic charge from the "phenol" ring to the "pyridine" ring. An increase of electron density in the "phenol" ring or a decrease of electron density in the "pyridine" ring will move the transition to lower energies.

Thus, in basic media the hydroxyl function dissociates and the formal negative charge on the oxygen atom will repel electrons into the other ring thereby facilitating the transition. Again, protonation of the nitrogen results in a formal positive charge on the nitrogen atom, which can attract electrons from the other ring, facilitating the transition. These shifts are observed experimentally. The shift to lower energies in the halogen derivatives may similarly be due to the π -electron donating power of the halogens rather than simply to an increase in the size of the π system.

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