ally, of σ-values for the *m*- and *p*- $\geqslant N^{+}$—H groups, which are indicated in Table II, where they can be compared with values derived from the aminopyridines.

Similar tautomeric equilibria, of course, arise in the 1-oxides of nicotinic and isonicotinic acid, in 3-hydroxypyridine and in the aminopyridines. These cases are not further discussed here since there appears to exist no question about the assignment of the *pK*'s to the various possible equilibria. Arguments of the type described in this paper lead to the assignments indicated in the preceding paper,[6] and are in agreement with expectations.

NOTE ADDED IN PROOF.—Since this paper was accepted for publication, Metzler and Snell[15] have reported an investigation of the tautomeric equilibrium between 3-hydroxypyridine and the corresponding zwitterion. Their data present a gratifying verification of the validity of the method proposed in the present paper. Let us denote 3-hydroxypyridine by 3-VI', its zwitterion by 3-VII', and its conjugate acid and base, respectively, by 3-VIII' and 3-V', in analogy with the similar compounds V–VIII. The method presented in this paper, together with known σ and ρ values,[16] then leads to the following *pK* values: 3-VIII' $\rightleftharpoons$ 3-VI', 5.30; 3-VIII' $\rightleftharpoons$ 3-VII', 5.42 and 3-VI' $\rightleftharpoons$ 3-V', 8.54. These values compare with 5.44, 5.37 and 8.26, respectively, reported by Metzler and Snell; the agreement is seen to be excellent, considering the uncertainties involved in the Hammett equation in general, and its application to heterocyclic compounds in particular. Metzler and Snell's value for the tautomeric equilibrium constant, $K = 1.17$, also compares favorably with our calculated value, $K = 0.76$. The data quoted are particularly gratifying since they seem to suggest that the substituent constants for groups such as 3-$\geqslant N^{+}H$ appear to have real significance. The data further permit calculation, for the *m*-O^{-}-group, of a value $\sigma = -0.54$, which seems very reasonable.

Acknowledgment.—The author acknowledges the skilled technical assistance of Mrs. Caroline Sasser.

CINCINNATI, OHIO

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(15) D. E. Metzler and E. E. Snell, THIS JOURNAL, **77**, 2431 (1955).

(16) See Table II, ref. 6 and H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

Tautomeric Equilibria. II. A Molecular Orbital Discussion of the Relative Stabilities of Pairs of Tautomers Involving Benzenoid and Quinoid Structures[1]

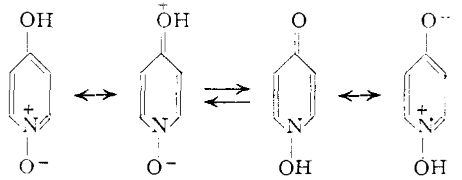
BY H. H. JAFFÉ

RECEIVED JANUARY 28, 1955

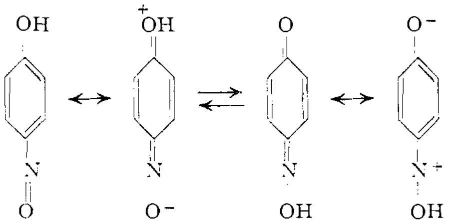
The difference in π-electron energy between each of the isomeric hydroxypyridine 1-oxides and the tautomeric N-hydroxypyridones, and between each of the isomeric nitrosophenols and the corresponding benzoquinonone monoximes has been calculated by molecular orbital theory, using a crude perturbation method. The hydroxypyridine 1-oxides and 3-nitrosophenol are found to be more stable than the corresponding N-hydroxy compounds, but *o*- and *p*-benzoquinone monoxime are more stable than the corresponding nitrosophenols. These conclusions are in agreement with experimental facts, as far as is known, with the possible exception of 2-hydroxypyridine 1-oxide.

Tautomerism between a compound involving benzenoid forms and its isomer involving a quinoid form as predominant resonance structures have frequently been discussed.[1,2] Whenever the quinoid compound[3] is found to be the more stable of a pair of tautomers, the question arises what characteristic of the quinoid compound can overcome the difference in resonance energy between benzenoid and quinoid compounds which, in general, is of the order of 20 kcal./mole.[4] As a contribution to this problem the present paper reports an investigation of the benzenoid and quinoid tautomers[3] of the isomeric hydroxypyridine 1-oxides (N-hydroxypyridones) and of the isomeric nitrosophenols (benzoquinone monoximes) by molecular orbital (MO) theory. In spite of its crude nature, the perturbation method of Coulson and Longuet-Higgins is used[5] since it makes the desired treatment especially simple.

The equilibria investigated are represented by formulas I–VIII and by the corresponding isomers in which the two functional groups are in the α and β (or *ortho* and *meta*) positions to each other. It should be noted that the structures written are only those considered most important, and that no



I II III IV



V VI VII VIII

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(1) Presented before the Division of Physical and Inorganic Chemistry at the 127th meeting of the American Chemical Society, Cincinnati, Ohio, April, 1955. For paper I, see H. H. Jaffé, THIS JOURNAL, **77**, 4445 (1955).

(2) *E.g.*, (a) E. Havinga and A. Schors, *Rec. trav. chim.*, **69**, 457 (1950), and references cited there. (b) G. E. Philbrook, paper presented before the Southeastern Section of the American Chemical Society, Birmingham, Alabama, October, 1954.

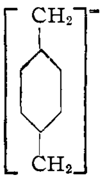
(3) We shall call "quinoid compound" the tautomer in which the quinoid structure is presumably the predominant resonance structure because it is the only structure not involving separation of charges. The other tautomer, in which the benzenoid structures presumably predominate, will be designated as "benzenoid compound."

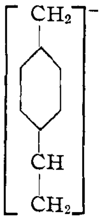
(4) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 69.

(5) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A191**, 39 (1947); **A192**, 16 (1947).

such important quinoid structures can be written for the β (or *meta*) compounds. The cases chosen are particularly amenable to treatment since, in each pair of tautomers, both compounds have an equal number of σ-bonds of each type; hence, to the approximation that the additivity of bond energies is valid, the only differences in σ-bond energies in the tautomeric pairs arise from the differences in bond lengths in benzenoid and quinoid forms. Since the change from one to the other of these forms involves shortening of some and lengthening of others of the σ-bonds, it is reasonable to assume that all such differences in σ-bond energies cancel, and accordingly we ascribe all energy differences to π-electron energies. Thus, the problem of the relative stabilities of these pairs of tautomers is reduced to a comparison of their π-electron energies. This procedure also implies the reasonable assumption that differences in entropy, in vibrational energy, and in solvation energy can be neglected.

Within the realm of the Coulson-Longuet-Higgins perturbation method,[5] each pair of tautomers is represented by a single unperturbed reference compound; thus, structures I to IV are represented by IX, and structures V to VIII by X. The π-electron energy $\mathcal{E}$ of the actual compounds (as distinguished from the reference compounds) are then given by[5]


IX


X

$$\mathcal{E} = \mathcal{E}^0 + \sum_r q_r\,\delta\,\alpha_r + \sum_{r<s} p_{rs}\,\delta\beta_{rs} \tag{1}$$

Here $\mathcal{E}^0$, q_r and p_{rs} are the π-electron energy, the charge density at atom r and the mobile bond order of bond r–s, respectively, in the reference compound, and the $\delta\alpha_r$ and $\delta\beta_{rs}$ are the differences in Coulomb and resonance integrals between actual and reference compounds, respectively. Consequently, the difference in π-electron energy between members of a pair of tautomers depends only on the q_r and p_{rs} in the common reference compound, and the differences $\Delta\alpha_r$ and $\Delta\beta_{rs}$ in Coulomb and resonance integrals, respectively, between corresponding atoms and bonds in the tautomers

$$\Delta\mathcal{E} = \sum_r q_r\,\Delta\alpha_r + \sum_{r<s} p_{rs}\,\Delta\beta_{rs} \tag{2}$$

The q_r and p_{rs} are evaluated readily[5,6]; the Coulomb and resonance integrals, however, produce major obstacles; their estimation will now be discussed.

Choice of Parameters.—It has long been apparent that the same Coulomb integral cannot be used for a single atomic species under different conditions. Thus, in the calculation of dipole moments, the nitrogen atom in pyrrole required a Coulomb integral ($\delta\alpha_N$) twice as large as the nitrogen atom in pyridine,[7] and the nitrogen atoms in pyridine and aniline require Coulomb integrals ($\delta\alpha_N$) of opposite sign.[8] Consequently it appears safe to conclude that Coulomb integrals should be chosen separately for any given atom in different surroundings. The "best" parameters should be those which lead to a set of MO's as nearly self-consistent as possible. In order to make such choices of parameters we propose to use resonance theory[4] to judge what resonance structures are probably most important in a given molecule, and to choose the parameters which appear, from empirical experience, best suited to these structures. This procedure is followed in the present paper, and the parameters so chosen are listed in Table I.

TABLE I

PARAMETERS USED FOR VARIOUS HETEROATOMS AND BONDS[a]

Parameter	Group	Value in β	Source
$\delta\alpha_O$	>C—OH	0.5	Ref. 8a
	=N—OH	0.7	[b]
	>C—O⁻	−1.0	Rough estimate from σ-value
	>N⁺—O⁻	1.0	Ref. 9
	>N⁺OH	0.7 (1.0)	Ref. 8a[c]
	>C=O, —N=O	1.0	Ref. 11b[d]
$\delta\alpha_N$	>N⁺—O⁻	2.0	Ref. 9
	>N⁺OH	3.2	From σ-value, *cf.* ref. 1
	>N-	1.2	Ref. 7, 8
	—N=O, =N—OH —N⁺OH	Difference 2.0[e]	Assumed
β_s	All bonds shown as single	0.6	Ref. 12
β_d	All bonds shown as double	1.2	Ref. 12
β	All benzenoid ring bonds	1.0	

[a] All parameters are rounded off to one decimal place, even where original papers report more places, since more places are certainly without significance. [b] From ref. 8a, corrected for the inductive effect of the N-atom. [c] The value in parentheses is derived from values in ref. 1. [d] Derived from Gold's values and β_d = 1.2. [e] Only the difference between the values for —N=O and –N⁺OH is needed. Any value <2.5 leads to reasonable results, and a value of 2.0 appears very reasonable.

For the phenolic OH– group we use the parameters derived from Hammett substituent constants.[8a] For an OH–

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(6) The MO's from which the q_r and the p_{rs} are calculated have been published as appendices to earlier papers (H. H. Jaffé, THIS JOURNAL, **76**, 5843 (1954); **77**, 274 (1955); ADI Documents No. 4308, 4349) or are given in an appendix to the present paper. The q_r and p_{rs} for all the compounds are also given in the appendix. This appendix has been deposited as Document number 4491 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

(7) L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

(8) (a) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279 (1952); (b) 1554 (1952); (c) P.-O. Löwdin, *ibid.*, **19**, 1323 (1951).

group attached to a nitrogen atom, $\delta\alpha_0$ is taken slightly larger to correct for the inductive effect of the nitrogen atom. For the $\geqslant N^+—O^-$– group, we use parameters similarly derived.[9] Reliable substituent constants for the O^-–group are not known[10]; however, there is no question that both σ_p and σ_m must have appreciable negative values. Accordingly, a negative Coulomb integral, and a resonance integral of the same order of magnitude as for OH are indicated. The Coulomb integral of oxygen in quinones has been discussed repeatedly[11]; Gold's work, in particular, is based on the same assumptions concerning the inductive effect as our own, and hence his value was accepted. Resonance integrals in quinones have also been discussed in detail,[12] and values of $\beta_d = 1.2\beta$ and $\beta_s = 0.6\beta$ appear most satisfactory. In accordance with the procedure used by the Italian workers, these values are used throughout for bonds indicated as double and single, respectively, in quinoid structures. It is noteworthy that our value for β for phenolic OH ($\beta = 0.57$)[8a] agrees closely with the β_s value of the Italian workers ($\beta_s = 0.58$).[12]

The Coulomb integrals for the various nitrogen atoms require some further comment. For threefold single bonded N-atoms (as in III) we use $\delta\alpha_N = 1.2$.[7,8] We assume $\delta\alpha_N$ for $\geqslant C–N^+–OH$ 2 β larger than for $\geqslant C—N{=}O$, and the latter equal to $\delta\alpha_N$ for $\geqslant C{=}N—OH$. For $\delta\alpha_N$ in $\geqslant N^+OH$ we use a value derived from substituent constants[1]; the same calculation leads to $\delta\alpha_0 = 1.0$ in $\geqslant N^+OH$. We report calculations for both $\delta\alpha_0 = 1.0$ and $= 0.7$ in this group.

The inductive effect is treated in the manner used in earlier papers,[8a,b,9] *i.e.*, by assigning to ring carbon atoms increments in Coulomb integral

$$\delta\alpha_r = 3^{-n_r}\,\delta\alpha_H \tag{3}$$

where n_r is the number of bonds between carbon atom r and the nearest heteroatom, for which the Coulomb integral is $\delta\alpha_H$.

Results and Discussion

The results of the calculations are summarized in Table II. In column I we present the effects of varying only the Coulomb integrals, in accordance with the common approximation of assuming all resonance integrals equal. In column II we list the results of the variation of the resonance integrals alone, and the combined effects are given in the last column. It should be noted that the variation of the resonance integrals barely affects the results for the pyridine 1-oxides, but largely balances the effects of the Coulomb integrals in 2- and 4-nitrosophenol.

TABLE II

DIFFERENCE IN π-ELECTRON ENERGIES BETWEEN TAUTOMER PAIRS[a]

Compound[b]	I[c]	II[d]	Total
4-HOC_5H_4NO	−0.88	−0.03	−0.91
3-HOC_5H_4NO	−1.41	0	−1.41
	(−0.94)[e]		(−0.94)[e]
2-HOC_5H_4NO	−1.16	+0.03	−1.13
4-HOC_6H_4NO	+0.70	−0.42	+0.28
3-HOC_6H_4NO	−0.37	−0.55	−0.92
2-HOC_6H_4NO	+0.64	−0.46	+0.18

[a] All energies are given in units of the benzene resonance integral $\beta \approx 20$ kcal./mole. A negative sign indicates that the phenolic (benzenoid) compound is more stable than the N-hydroxy (quinoid) tautomer; a positive sign indicates the opposite conclusion. [b] Only the phenolic (benzenoid) isomer is given. [c] Using the first term in equation 2 only. [d] Using the second term in equation 2 only. [e] The first value was obtained using $\delta\alpha_0$ ($\geqslant N^+OH$) = 0.7, the second using 1.0; *cf*. footnote *c*, Table I.

According to Table II the phenolic tautomers are more stable than their N-hydroxy isomers in both series of compounds treated when the functional groups are *meta* (β) to each other. This result, of course, was anticipated since no quinoid resonance structures can be written without "long bonds." Assuming a value of $\beta \approx 20$ kcal./mole, which is generally accepted in considerations of thermochemical data,[4] we obtain an energy difference between the *meta* phenolic compounds and their N-hydroxy tautomers of about 20–30 kcal./mole. This figure appears to be of the right order of magnitude, although it may be a slight overestimate.

Further, Table II suggests that 2- and 4-hydroxypyridine 1-oxide should be more stable than the tautomeric N-hydroxypyridones by about 20 kcal./mole. Qualitatively this conclusion agrees with experimental fact for the 4-isomer[1]; for the 2-isomer, however, Shaw believes to have demonstrated the opposite stability relation.[13] Although Shaw's conclusion is based exclusively on spectroscopic data, the evidence appears to be conclusive. No explanation for this discrepancy will be proposed. It seems clear, however, that the energy difference of 20 kcal./mole is an overestimate even for the 4-isomer.

Finally, Table II indicates that *o*- and *p*-benzoquinone monoxime are more stable than the corresponding tautomeric nitrosophenols by 4–6 kcal./mole. This conclusion is in agreement with Philbrook's results on the 4-isomer[2b]; no reliable information on the 2-isomer appears to be available.

In conclusion, we must examine why it is possible for the "quinoid" forms, at least in some cases, to overcome the benzenoid resonance energy. First, consideration of resonance between structures such as I ↔ II, III ↔ IV, V ↔ VI and VII ↔ VIII suggests that the quinoid structures II and VI probably make appreciable contributions to the "benzenoid" compounds (I and V), and that the "benzenoid" structures IV and VIII probably make appreciable contributions to the "quinoid" compounds (III and VII). Comparison with similar structures for benzene and benzoquinone indicates that this type of resonance is of much greater importance in the compounds discussed in this paper than in unsubstituted benzene and in simple quinones. Consequently we may conclude that the difference in resonance energy between benzenoid and quinoid compounds is not nearly as great as has frequently been assumed.

Secondly, we have seen above that each pair of tautomers has a common reference compound, and the difference in π-electron energy therefore depends only on the perturbation involved in passing from the reference compound to the two tautomers. Table II indicates that the $\delta\alpha$ terms make the greatest contribution to the differences in π-electron energies. The most pronounced effect of assigning realistic Coulomb integrals to various atoms is, of course, the effect on the distribution of π-electrons. Hence we may conclude that the quinoid structures, when they are more stable than the tauto-

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(9) H. H. Jaffé, THIS JOURNAL, **76**, 3529 (1954).

(10) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(11) (a) C. A. Coulson, *Trans. Faraday Soc.*, **42**, 106 (1946); (b) V. Gold, *ibid.*, **46**, 109 (1950).

(12) G. B. Bonino and M. Rolla, *Atti. accad. Nat. Lincei, Rend., Classe Sci. fis. mat. e nat.*, [8] **5**, 220 (1948); M. Rolla and A. M. Mariangelli, *Boll. sci. fac. chim. ind. Bologna*, 28 (1948).

(13) E. Shaw, THIS JOURNAL, **71**, 67 (1949).

meric benzenoid compounds, permit an energetically, especially favorable distribution of charges.

Acknowledgments.—Several interesting discussions with Dr. G. E. Philbrook of the University of Georgia are gratefully acknowledged; they provided much of the stimulation needed to attack this problem.

CINCINNATI 21, OHIO

[CONTRIBUTION FROM THE VENEREAL DISEASE EXPERIMENTAL LABORATORY, U. S. PUBLIC HEALTH SERVICE, SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF NORTH CAROLINA]

The Ultraviolet Absorption Spectra of Substituted Pyridine 1-Oxides and their Conjugate Acids

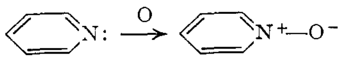
BY H. H. JAFFÉ[1]

RECEIVED SEPTEMBER 27, 1954

The ultraviolet absorption spectra of pyridine 1-oxide and of its conjugate acid, 1-hydroxypyridinium ion, have been determined in water and in 50% sulfuric acid, respectively, and are compared with the spectra of pyridine and pyridinium ion The effect of substituents in the 3- and 4-position on the spectra of pyridine 1-oxide and of its conjugate acid are determined. The spectra of isoquinoline 2-oxide and of its conjugate acid are also reported.

The ultraviolet absorption spectrum of pyridine is well known.[2] Its most outstanding feature is a band near 256 mμ with a molar extinction coefficient ϵ_{max} 2.66 × 10^3, both values in aqueous solution. This band shows a well defined vibrational structure. In acidic solution, where the species present is pyridinium ion, the wave length of this band is unaltered, but ϵ_{max} is increased twofold, to 5.32 × 10^3, and the vibrational structure is greatly decreased.[2a] The difference between the two spectra must be ascribed to the tying up of the unshared electron pair of the nitrogen atom, and to the introduction of the formal positive charge at this atom.

An alternate way of tying up the lone pair consists of oxidizing pyridine to its 1-oxide.



The spectrum of the latter compound is shown in Fig. 1 (*cf.* Table I). It shows a single very intense band, devoid of all vibrational structure, at almost the same wave length as the bands of pyridine and pyridinium ion, but of much higher ϵ_{max}. The intensity difference between pyridinium ion and pyridine 1-oxide can be understood since the latter compound has an appreciably larger conjugated system, due to the contributions of structures of the types I and II.[3] The spectrum also shows that a

I II

further band is present at the far ultraviolet end of the range accessible with the available equipment. The band maximum probably lies at 205 mμ, and has a molar extinction of about 1.7 × 10^4.

Introduction of various substituents in the 3-position does not greatly affect either the wave length or the intensity of the 254 mμ band of pyridine 1-oxide. Substituents in the 4-position have a somewhat larger effect in increasing the intensity of the absorption, up to almost twofold, and leading to a red-shift of up to 26 mμ (*cf.* Table I). The shorter wave length band appears to be somewhat more susceptible to effects of substituents, particularly those in the 3-position.

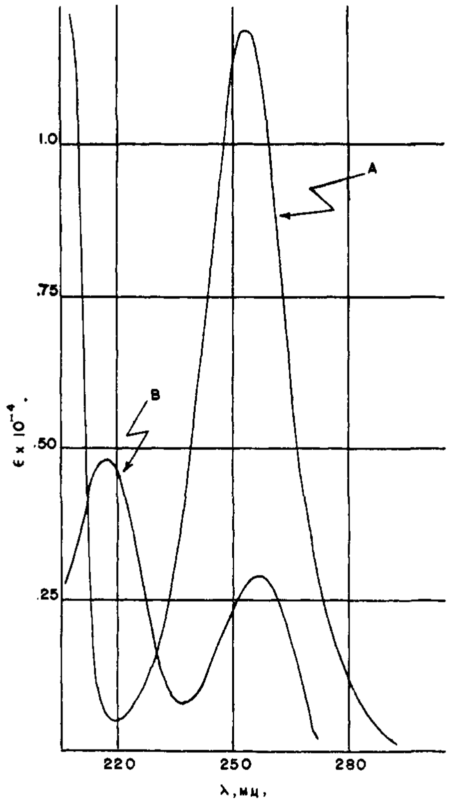


Fig. 1.—The spectra of pyridine 1-oxide in water (A), and of 1-hydroxypyridinium ion in 62% sulfuric acid (B).

As commonly found in spectroscopic investigations, the nitro group exerts a profound effect; the spectrum of 4-nitropyridine 1-oxide is shown in Fig. 2.

From the intensity, from the effect of substituents on the wave length (red-shift), and from the

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[1] Department of Chemistry, University of Cincinnati, Cincinnati 21, Ohio.

[2] (a) E. B. Hughes, H. H. G. Jellinek and B. A. Ambrose, *J. Phys. Colloid Chem.*, **53**, 410 (1949); (b) *cf.* also H. P. Stephenson, *J. Chem. Phys.*, **22**, 1077 (1954).

[3] H. H. Jaffé, THIS JOURNAL, **76**, 3527 (1954).