of TS with the adjacent long chains of stearic acid is undoubtedly responsible for the compatibility. Stearic acid probably neither aids nor hinders packing of TS molecules. The thiadiazole ring is sufficiently small or hidden that it does not interfere.

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WHITING, INDIANA

[CONTRIBUTION FROM THE VENABLE LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Ultraviolet Absorption Spectra and the Dissociation Constants of the Monochloroquinolines and the Monomethylquinolines

BY SAMUEL B. KNIGHT, R. H. WALLICK AND CAROLYN BALCH

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The ultraviolet absorption spectra of all seven of the monochloroquinolines and the 2-, 3-, 4-, 6-, 7- and 8-monomethylquinolines have been determined in 95% ethanol, 10% ethanol and 10% ethanol that is 0.01 molar in hydrochloric acid. The changes in intensity and the shifts in wave lengths of the maxima of the monochloroquinolines have been correlated with molecular dimensions. The shifts in the wave lengths for the methylquinolines cannot be associated with the dimensions of the molecules as was the case with the haloquinolines studied. The dissociation constants of the monochloro- and monomethylquinolines have also been determined from spectral data. Possible reasons, based on electron densities at the nitrogen atom, as influenced by the various substituents, are given for the order of basic strengths.

The data presented in this paper are the results of a continuation of the work done previously in this Laboratory on the ultraviolet absorption spectra of the monosubstituted quinolines.[1-3]

It has been shown in one of these papers[3] that the spectral shifts of the monobromo- and monofluoroquinolines can be correlated with molecular dimensions. In the present work the spectra of the chloroquinolines and the methylquinolines have been determined in 95% ethanol, 10% ethanol and 10% ethanol that is 0.01 molar in hydrochloric acid.

The dissociation constants of the chloroquinolines and the methylquinolines were also determined from spectral measurements.

Discussion

The shifts of wave length and the changes in the molar extinction coefficients for the two near ultraviolet absorption peaks of the chloroquinolines follow the same generalizations as those given in a previous paper for the other haloquinolines.[3] From Table I it can be seen that the greater changes in the longer wave length peak, the B band, come about when the chlorine is in the 2-, 3-, 6- or 7-position. Substitution in the 4-, 5- or 8-position produces the greater changes in the shorter wave length peak, the E_2 band. These displacements are explained if one associates the great extension of the molecule with the longer wave length peak and the smaller extension with the next shorter wave length peak. Substitution which will increase the length of the field in which the oscillating electron is free to move will lower the energy of that electron. The wave length of the peak arising from this transition will be shifted to longer wave lengths. For a clearer picture reference[3] should be consulted.

In the study of light absorption in the methylquinoline series one must recognize the possibility

TABLE I

SPECTRAL DATA OF THE CHLOROQUINOLINES IN 10% ETHANOL

Compound	B Band λmax, Å.	B Band εmax	B Band Δλ	E_2 Band λmax, Å.	E_2 Band εmax	E_2 Band Δλ
2-Chloroquinoline	3180	4610	50	2820	3320	60
3-Chloroquinoline	3230	3560	100	2830	3060	70
4-Chloroquinoline	3160	2850	30	2890	4900	130
5-Chloroquinoline	3170	3170	40	2920	4640	160
6-Chloroquinoline	3190	3500	60	2760	3650	0
7-Chloroquinoline	3190	3670	60	2790	3560	30
8-Chloroquinoline	3150	2990	20	2920	4500	160
Quinoline	3130	3410		2760	3590	

of hyperconjugation of the methyl group. Mulliken *et al.*,[4] and Coulson[5] give the structure of the methyl group as $-C{\equiv}H_3$ where the three hydrogens are treated as a group. The molecular orbitals of this group of hydrogens give an unsymmetrical distribution of electron density above and below the plane of the ring system with a node in the plane. This cloud resembles the π-electron configuration and may interact with the ring. Hyperconjugation leads one to expect a lowering of the energy necessary for the electronic transitions in quinoline resulting in bathochromic shifts. The data in Table II show that there is a red shift for the two absorption

TABLE II

SPECTRAL DATA OF THE METHYLQUINOLINES IN 10% ETHANOL

Compound	B Band λmax, Å.	B Band εmax	B Band Δλ	E_2 Band λmax, Å.	E_2 Band εmax	E_2 Band Δλ
2-Methylquinoline	3150	3860	20	2790	3200	30
3-Methylquinoline	3180	3120	50	2860	3350	100
4-Methylquinoline	3130	2730	0	2830	4530	70
6-Methylquinoline	3170	2330	40	2850	2340	90
7-Methylquinoline	3180	2400	50	2920	2170	160
8-Methylquinoline	3140	2650	10	2920	3750	160

(1) W. K. Miller, S. B. Knight and A. Roe, THIS JOURNAL, **72**, 1629 (1950).

(2) W. K. Miller, S. B. Knight and A. Roe, *ibid.*, **72**, 4763 (1950).

(3) S. B. Knight, R. H. Wallick and J. Bowen, *ibid.*, **76**, 3780 (1954).

(4) R. S. Mulliken, C. A. Rieke and W. G. Brown, *ibid.*, **63**, 4 (1941).

(5) C. A. Coulson, *Quart. Rev.*, **I**, 144 (1947).

peaks of all the methylquinolines except those of the 4-methylquinoline which shows no shift in the B band.

The shifts in wave length for the methylquinolines cannot be associated with the dimensions of the molecule as was the case with the haloquinolines studied. The interaction of the methyl group with the ring nitrogen must completely obscure any selective absorption due to orientation of the molecule.

In Table III are listed the wave lengths of the E_2 absorption peaks and also the molar extinction coefficients for these peaks for the 2-, 4-, 6-, 7- and 8-methylquinolines found in 10% ethanol, 95% ethanol and isoöctane (data for the 8-methylquinoline in isoöctane were not available). The values for isooctane are those of Friedel and Orchin.[6]

TABLE III

SPECTRAL DATA FOR THE E_2 BAND OF THE METHYLQUINOLINES IN VARIOUS SOLVENTS

Compound	10% Ethanol λmax, Å.	10% Ethanol εmax	95% Ethanol λmax, Å.	95% Ethanol εmax	Isoöctane λmax, Å.	Isoöctane εmax
2-Methylquinoline	2790	3200	2730	3450	2700	3720
4-Methylquinoline	2830	4530	2800	4750	2740	4790
6-Methylquinoline	2850	2340	2790	2530	2700	3390
7-Methylquinoline	2920	2170	2840	3320	2760	3310
8-Methylquinoline	2920	3750	2910	3590	..	..

In solutions which were 0.01 M in acid and 10% in ethanol the shorter wave length peak disappears and the longer wave length peak becomes more intense but shows no shift in wave length from solutions which are not acidic. At first observation the disappearance of the one peak seems to indicate the possibility of an $n \rightarrow \pi$ transition.[7] However Kaska[8] states that for an $n \rightarrow \pi$ transition the peak moves to a much shorter wave length and also McConnell[9] says that for all $n \rightarrow \pi$ transitions studied there is a blue shift in the solvent series paraffin, alcohol, water and acid.

On looking at the data in Table III, however, one sees that the shift in the E_2 wave length is to the red in the same series as that of McConnell. Furthermore studies of solutions of varying pH show that this peak moves slowly to red and eventually becomes obscured by the longer wave length peak. At the same time that the bathochromic shift takes place the intensity becomes less; however, since it is covered up by the B band it is not known whether it eventually disappears completely or not. This does not prove that the transition causing the absorption is not $n \rightarrow \pi$ but must be $\pi \rightarrow \pi$. The energy necessary for the transition is lowered but the probability of the transition is also lowered simultaneously as the concentration of hydronium ion is increased.

The change in wave length in the B band peak is within experimental error and remains practically constant in this solvent series.

The Dissociation Constants of the Methylquinolines.—From the consideration of hyperconjugation already discussed it is seen that the methyl group is electropositive, donating electrons to the ring system. In the case of the methylquinolines the basic character should be enhanced if resonance structures can be drawn which would cause an increase in electron density at the nitrogen.

The 2-, 4-, 5- and 7-methylquinolines have resonance forms which can cause an accumulation of electrons on the nitrogen. These then should be the strong bases. The 3-, 6- and 8-methylquinolines have no such resonance forms and thus should be weak bases.

In Table IV the K_b's as determined by the method of Stenstrom and Goldsmith[10] are given and it is seen that the experimental results bear out the predictions. The 5-methylquinoline was not available for study.

TABLE IV

DISSOCIATION CONSTANTS OF THE METHYLQUINOLINES AT 25°

Compound	Dissociation constants, K_b
2-Methylquinoline	$2.6, 2.9, 2.6, 2.6 \times 10^{-9}$
3-Methylquinoline	$1.9, 1.9 \times 10^{-10}$
4-Methylquinoline	$2.0, 2.2, 2.2, 2.2 \times 10^{-9}$
6-Methylquinoline	$7.6, 7.6, 7.9, 7.8 \times 10^{-10}$
7-Methylquinoline	$1.0, 1.0, 1.2, 1.1 \times 10^{-9}$
8-Methylquinoline	$5.0, 4.3, 4.2, 4.4 \times 10^{-10}$

A methyl group on the ring with the nitrogen influences the basic nature more than the same group does on the benzenoid ring. Thus the strong bases 2- and 4-methylquinolines are stronger bases than any of the others, and the weak base 3-methylquinoline is the weakest base of all.

The Dissociation Constants of the Chloroquinolines.—All of the dissociation constants for the chloroquinolines show that these compounds are weaker bases than quinoline itself. This is certainly to be expected from the fact that chlorine is electronegative and by an inductive effect causes a drain of electrons from the ring. The electron density at the nitrogen is smaller for a chloroquinoline than for quinoline with the result that the hydronium ion is attracted less and is held less firmly on the substituted compound. This induction is greater the nearer the chlorine is to the nitrogen. The effect is particularly strong for substitution on the pyridinoid ring. The K_b values listed in Table V show that the basic strength increases as the distance between the nitrogen and the substituted carbon increases. The 3- and the 8-chloroquinolines have nearly the same value for the dissociation con-

TABLE V

DISSOCIATION CONSTANTS OF THE CHLOROQUINOLINES AT 25°

Compound	Dissociation constants
2-Chloroquinoline	.....
3-Chloroquinoline	$2.2, 2.1, 2.5, 2.5 \times 10^{-12}$
4-Chloroquinoline	$2.6, 2.5, 2.8, 2.6 \times 10^{-11}$
5-Chloroquinoline	$2.5, 2.5, 2.6, 2.2 \times 10^{-11}$
6-Chloroquinoline	$1.0, 1.0, 1.0, 1.1 \times 10^{-11}$
7-Chloroquinoline	$3.7, 3.8, 3.8, 4.2 \times 10^{-11}$
8-Chloroquinoline	$7.1, 7.1, 7.6, 7.0 \times 10^{-12}$

(6) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.

(7) V. R. Platt, *J. Chem. Phys.*, **19**, 101 (1951).

(8) M. Kaska, *Disc. Faraday Soc.*, **9**, 14 (1950).

(9) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(10) W. Stenstrom and N. Goldsmith, *J. Phys. Chem.*, **30**, 1683 (1926).

stant since both have approximately the same distance between the chlorine and nitrogen. The 5-, 6- and 7-chloroquinolines are the strongest bases in the series for in these the chlorine has the least effect upon the electron density at the nitrogen. The 2-chloroquinoline is such a weak base that a constant could not be determined.

Experimental

Absorption Spectra.—The spectra were determined as was reported in the previous paper[3] using a Beckman Model DU quartz spectrophotometer. The concentrations were approximately 0.0002 molar.

Dissociation Constants.—All *p*H measurements were made with a Leeds and Northrup *p*H indicator, Model No. 7664 with glass and saturated calomel electrodes. All measurements were made in a constant temperature room at 25°.

Materials.—The 4-, 6-, 7- and 8-methylquinolines and the 2- and 6-chloroquinolines were Eastman Kodak Co. products and were redistilled before use. The 2- and 3-methylquinolines and 3-, 4-, 5-, 7- and 8-chloroquinolines were prepared in this Laboratory.

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CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES]

Further Studies of the Interactions of Polar Gases with Solid Proteins and Some Simple Organic Compounds[1-3]

BY JERROLD M. SEEHOF AND SIDNEY W. BENSON

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Studies of the stoichiometric binding of HCl, NH_3, BF_3 and CH_3NH_2 by solid proteins have been extended to a varied series of proteins and concomitantly to some model organic compounds for purposes of comparison. As reported earlier HCl is bound to arginine, histidine and lysine. NH_3 is hardly bound at all while CH_3NH_2 binds less than the expected number of free acid groups. BF_3 can add to even weak Lewis bases and its binding is strongly pressure dependent. In all cases but especially with BF_3, there is a very pronounced effect of particle dispersity indicating diffusion controlled reactions. Strong and weak basic groups can be distinguished in all cases by techniques of back titration. The evidence points to a Zwitterion structure for the residues such that the strong bases are present as $RCOO^{-1}$, the corresponding acids being RNH_3^{+1}. A smaller base strength of the peptide group is found in proteins compared to that in Nylon and is compatible with the α-helix structure for proteins.

Introduction

In earlier studies reported from these laboratories[4-7] it has been shown that the interactions of acidic and basic gases with solid proteins showed a stoichiometric character which could be interpreted in terms of a chemical reaction of these gases with the basic and acidic residue groups in the protein molecule leading to compound formation. Because these reactions are complex and are accompanied by a considerable amount of physical sorption it was decided to extend the work to a large number of proteins of differing structure to gain some information on the important structural features of the interactions. For these purposes the proteins chosen were egg albumin, bovine serum albumin, casein, fibrin, edestin, gliadin, gelatin, lactalbumin, β-lactoglobin, zinc insulin, silk fibroin and pepsin. To aid in the interpretation of the results it was further decided to make a parallel series of studies on some simple organic solids. Glycine, glycyl-glycine, Nylon, histidine, sebacic acid and cetyl alcohol were the model substances chosen for this comparison. The gases used were those already studied in varying detail earlier, HCl, NH_3, CH_3NH_2 and BF_3. Finally because of the related interest in denaturation, heat denatured (coagulated) samples of egg albumin and bovine serum albumin were also included in the studies.

As will be evident from the following discussion, the results are in many cases incomplete and in some cases appear to present conflicting or at least ambiguous features. The results with BF_3 are of a preliminary nature and further work (some of which is now in progress in these laboratories) will be required before a coherent picture of the behavior of this gas with proteins can be obtained. Despite these shortcomings the results are extremely interesting in their implications for the chemical reactivity of the residue groups in solid proteins and indicate a considerably greater coherence of properties than had earlier been supposed.

Experimental Procedure

The details of the preparation of the proteins and gases have been given in earlier papers and will not be repeated here.[8] Similarly the apparatus and techniques of measurement have been described elsewhere.

Except where otherwise noted the temperatures for all the studies were ambient room temperatures (20–26°) it having been shown earlier that the results were not sensitive to temperature changes of this magnitude.

The materials used in the study were either crystalline (cryst.) spray-frozen (SF) or in the case of a number of insoluble substances, water swollen (Sw) and then frozen at Dry Ice or liquid nitrogen temperatures and vacuum dried.

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(1) This work represents in part material taken from the doctoral thesis of J. M. Seehof.

(2) The authors are indebted to the National Institutes of Health for a grant (G-3541) under the Public Health Service in support of the present work.

(3) Some of the material in this paper was presented at the Spring Meeting of the American Chemical Society held in Los Angeles, April 1953.

(4) S. W. Benson and J. M. Seehof, THIS JOURNAL, **73**, 5053 (1951).

(5) J. M. Seehof, B. Keilin and S. W. Benson, *ibid.*, **75**, 2427 (1953).

(6) S. W. Benson and J. M. Seehof, *ibid.*, **75**, 3925 (1953).

(7) S. W. Benson, R. L. Altman, R. L. Richardson and J. M. Seehof, *ibid.*, **75**, 6040 (1953).

(8) The insulin used in the present work was very generously provided by Eli Lilly and Company, E. R. Squibb and Sons and Sharpe and Dohme to all of whom we are much indebted.