For two different reaction times. t_1 and t_2

$$k_1t_1 = -\ln\left(1 - \frac{Q_1}{a}\right) \text{ and } k_1t_2 = \ln\left(1 - \frac{Q_2}{a}\right)$$

$$t_2 \ln\left(1 - \frac{Q_1}{a}\right) = t_1 \ln\left(1 - \frac{Q_2}{a}\right)$$

$$1 - \frac{Q_2}{a} = \left(1 - \frac{Q_1}{a}\right)^{t_2/t_1}$$

Take $$t_2/t_1 = 2$$

$$1 - \frac{1}{a}Q_2 = \left(1 - \frac{1}{a}Q_1\right)^2$$

$$a = \frac{Q_1}{2 - Q_2/Q_1}$$

for points t_1, Q_1 and $2t_1$, Q_2.

Similarly it can be shown that

$$a = \frac{2Q_1}{3\sqrt{\frac{4Q_2}{Q_1}} - 3}$$

for points t_1, Q_1 and 3 t_1, Q_2 by setting $t_2/t_1 = 3$ in the above derivation.

Acknowledgment.—The author wishes to thank Dr. Benjamin Makower for many helpful discussions during the course of this work.

ALBANY, CALIF.

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

The Ultraviolet Absorption Spectra and the Dissociation Constants of the Monobromoquinolines

BY SAMUEL B. KNIGHT, R. H. WALLICK AND JACQUELINE BOWEN

RECEIVED JANUARY 7, 1954

The ultraviolet absorption spectra of the 2-, 3-, 5-, 6-, 7- and 8-monobromoquinolines 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 length of the maxima of the monobromo- and monofluoroquinolines have been correlated with molecular dimensions. The dissociation constants of the monobromoquinolines 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.

In extending the studies done in this Laboratory on the ultraviolet absorption spectra of the monohaloquinolines,[1] the 2-, 3-, 5-, 6-, 7- and 8-monobromoquinolines have been prepared[2] and their absorption spectra have been determined in 95% ethanol, 10% ethanol, and 10% ethanol that is 0.01 molar in hydrochloric acid. The 4-bromo-isomer proved to be unstable so that measurements were impossible.

The dissociation constants of the monobromoquinolines were also determined from spectral data, and there follows a discussion of the possible reasons for results from these and other measurements that have been made

Discussion

In discussing the spectra of these compounds we shall designate the absorption bands as B for the first band and E_2 for the second, following the terminology of Braude.[3] The B band is forbidden in a symmetrical molecule but a weak absorption is found due to unsymmetrical vibrations in the plane of the ring. The E_2 band comes from π-electron migration so that two electrons are placed on one atom in the ring. The E_2 band corresponds to the N → V transition of Mulliken.[4] The intensity of this band was shown by Sklar[5] to be high for benzene (2600 Å.) since it is not forbidden if polar structures are included in the calculations.

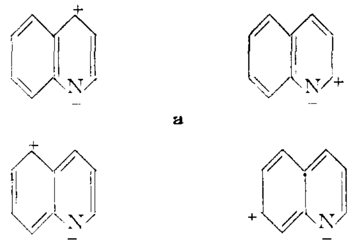

Fig. 1.

We shall consider naphthalene as the parent molecule and the quinolines as derivatives of this compound. The transition giving rise to the B band in naphthalene is N → V and is forbidden as shown from its low transition probability. This band is designated $'A$–$'L_b$ by Platt.[6] In quinolines and in the haloquinolines studied, the B band intensity is high and it follows that this is an allowed transition. Mulliken[7] states that in a compound such as pyridine where the ring symmetry is destroyed there is a transfer of the larger N → V energy to the transitions N → 'B1u and N → 'B2u which are forbidden in benzene.[5] This transfer increases the intensity of these bands.

In quinoline the B band has become an allowed N → V transition in an analogous way and ϵ_{max} shows a tenfold increase over that for naphthalene.

The ionic forms of quinoline contributing to the E_2 band are shown in Fig. 1.

These forms arise from π-electron migration from the ring onto the nitrogen atom. The nitrogen could not donate electrons to the ring since the only electrons available are the non-bonding 2s electrons. They have no nodes in the plane of the ring and therefore cannot interact with the plane of

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(1) (a) W. K. Miller, S. B. Knight and A. Roe, THIS JOURNAL, **72**, 1629 (1950); (b) *ibid.*, **72**, 4763 (1950).

(2) Preparations by Arthur Roe and his students.

(3) E. A. Braude, "Chemistry of Carbon Compounds," edited by Rodd, Elsevier Publishing Co., Amsterdam, Holland, 1951, Vol. I, pt. A, Chap. 7, p. 71.

(4) R. S. Mulliken, *J. Chem. Phys.*, **7**, 20 (1939).

(5) H. L. Sklar, *ibid.*, **5**, 669 (1937).

(6) J. R. Platt, *ibid.*, **17**, 484 (1949).

(7) R. S. Mulliken, *ibid.*, **7**, 353 (1939).

the ring unless excited to the sp state. This hybridization takes place only on nitrogen in the ammonia type molecules.

The nitrogen in the ring produces a stabilizing effect for the structures in Fig. 1a over the other forms. The structures should be the main contributing forms of quinoline for the $N \rightarrow V$ transition. In naphthalene there is no stabilization and the increased resonance of all forms contribute to the absorption with the result that $\epsilon_{\max}$ for naphthalene is stronger than that for quinoline.

Lewis and Calvin[8] show that the oscillations of a vibrating molecule can be shown to be equivalent to a simple oscillation of quasi-harmonic motion. In a planar molecule the restoring force constant, k, may be different in different directions. Plotted as a vector, k then makes an ellipse where k is a maximum in the x direction and a minimum in the y direction. The oscillations of the molecule then resolve themselves into independent oscillations of a frequency νx and νy. If a planar molecule has no center of symmetry, two fundamental electron bands are found, one of longer wave length than the other. The longer wave lengths are associated with the larger extension of the molecule.

Platt[9] also states that the B band exhibits a red shift with increasing chain length and is therefore longitudinally polarized along an axis of symmetry. He also says that the E_2 band exhibits a bathochromic shift as molecular width increases and that the intensity increases with substitutions which increase molecular width. This band is then transversely polarized.

In Table I are listed the maximum molar extinction coefficients, the wave lengths of these maxima and the change in wave length, $\Delta\lambda$, of the substituted quinolines from that of pure quinoline. Also are listed values for the fluoroquinolines.

TABLE I

SPECTRAL DATA OF SOME QUINOLINES AND NAPHTHALENES

The values for the quinolines were determined in 10% ethanol.

	B Band			E_2 Band		
Compound	$\lambda_{\max}$, Å.	$\epsilon_{\max}$	$\Delta\lambda$	$\lambda_{\max}$, Å.	$\epsilon_{\max}$	$\Delta\lambda$
Naphthalene[a]	3140	222		2750	6100	
α-Bromonaphthalene[b]	3200	160		2800	5010	
β-Bromonaphthalene	3200	250		2780	3160	
Quinoline[c]	3130	3410		2760	3590	
2-Fluoroquinoline	3120	2880	−10	2700	3810	−60
3-Fluoroquinoline	3190	3520	60	2840	3180	80
5-Fluoroquinoline	3140	1850	10	2850	3180	90
6-Fluoroquinoline	3160	3740	30	2700	3820	−60
7-Fluoroquinoline	3160	3800	30	2700	3150	−60
8-Fluoroquinoline	3130	1670	0	2840	3300	80
2-Bromoquinoline	3190	4160	60	2770	3420	10
3-Bromoquinoline	3230	3220	100	2790	3380	30
5-Bromoquinoline	3170	2890	40	2930	4960	170
6-Bromoquinoline	3200	3380	70	2730	3810	−30
7-Bromoquinoline	3200	3810	70	2690	4040	−70
8-Bromoquinoline	3150	2900	20	2910	4960	150

[a] Values for naphthalene API curves 132 (Sun Oil Company). [b] Values for bromonaphthalenes, I.C.T., curves Fig. 16, Vol. V, 363. [c] Values for fluoroquinolines from W. K. Miller, S. B. Knight and A. Roe, THIS JOURNAL, **72**, 1629 (1950).

By drawing scale diagrams of naphthalene and the quinolines (Fig. 2) we can determine the extension of the molecule along the x and y axes.

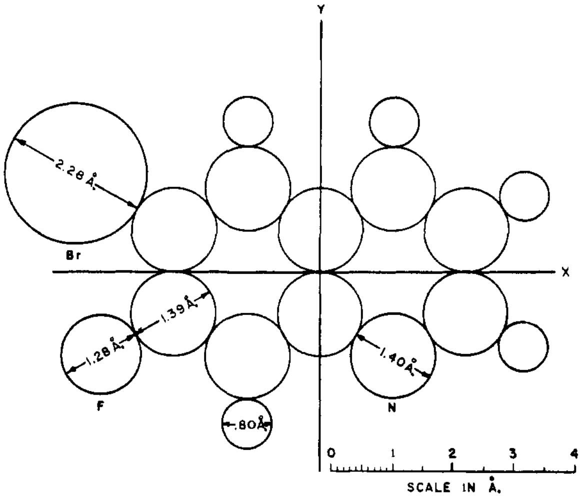

Figure 2.

From considerations above, the greater projection along the x axis of the molecule should produce the greater shift to the red in $\lambda_{\max}$ B, and $\epsilon_{\max}$ B should be larger. For a large projection on the y axis the greater shift should be observed in the $\lambda_{\max}$ E_2 and $\epsilon_{\max}$ E_2.

We have used the bromonaphthalenes for comparison with the bromoquinolines. $\lambda_{\max}$ for the bromonaphthalenes is higher than for naphthalene since the electron-donating properties of the bromine atom allow increased resonance with a decrease in the energy required for transition. Substitution in the α-position produces the greater shift in $\lambda_{\max}$ E_2 and also the greater $\epsilon_{\max}$. In the β-position the bromine produces no detectable shift in $\lambda_{\max}$ B over the α-isomer, but $\epsilon_{\max}$ is higher than for α-bromonaphthalene. These results are explained by the above considerations of molecular projection.

In the fluoro- and bromoquinoline series, the 2-, 3-, 6- and 7-positions have larger values for the x projection than the 4-, 5- and 8-isomers, while in the y direction the reverse is true. From this it would be expected that in the B band the 2-, 3-, 6- and 7-substitutions should produce larger wave length shifts and higher $\epsilon_{\max}$ values than the 5-, 7- and 8-positions. Conversely, in the E_2 band the 2-, 3-, 6- and 7-positions should have smaller wave length shifts and $\epsilon_{\max}$ changes than the 4-, 5- and 8-positions. In Figs. 3 and 4 plots of $\Delta\lambda$ *vs.* positions of bromine and fluorine for the B and E_2 bands show that the predicted shifts are followed closely when the substituent is on the benzenoid ring. From Table I it can be seen that $\epsilon_{\max}$ for both bands follow the predictions when the halogen is on the benzenoid ring with the exceptions of the $\epsilon_{\max}$ E_2 for the 5- and 6-fluoroquinolines where the order seems reversed. The shifts are not quite so pronounced in the fluoro series as in the bromo since, of course, the changes in molecular dimensions are not so great.

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(8) G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 273 (1939).

(9) J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).

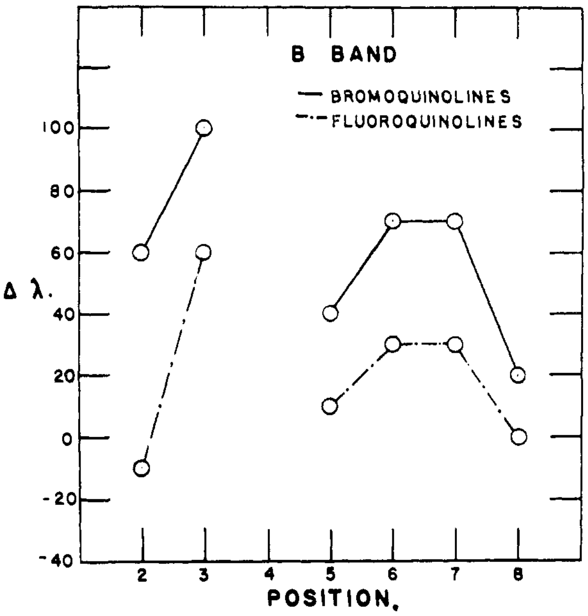

Figure 3.

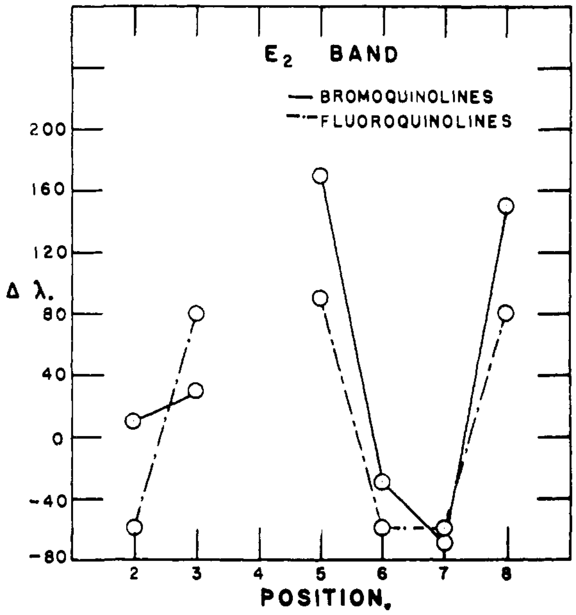

Figure 4.

When the substituent is on the heterocyclic ring this generalization seems not to be followed. In these cases, however, there are more chances for interaction of the substituent group with the nitrogen in the ring. The changes due to molecular dimension changes are masked by changes due to electron shifts since it must be remembered that the changes due to size may be thought of as being superimposed on the shifts of λ_{max} and ϵ_{max} due to electron rearrangements and ionic formations. These changes due to electron shifts are predominant but should be nearly constant for structurally similar compounds.

In the 0.01 *M* acid solutions all the compounds studied exhibit a marked decrease in ϵ_{max} E_2 and an increase in ϵ_{max} B. A proton is attached to the nitrogen atom in these solutions, which, though producing a larger inductive effect due to the positive charge, also prevents migration of the π-electrons onto the nitrogen. The absorption band E_2 is then reduced to an extremely low value. The inductive effect of the proton however causes a large displacement of electrons along the bond between the carbon and nitrogen. The ϵ_{max} for the B bond is doubled in these solutions.

The slight changes in the curves for these compounds in 95% and 10% alcohol are due to solvation differences.

Ionization Constants

The basic ionization constant of the bromoquinolines were measured in the manner of Miller and Roe.[1b] Various solutions of the quinolines were made up to different *p*H's. The molar extinction coefficients of each of the solutions were determined at the two wave lengths at which ϵ shows the greater change in going from acidic to basic solutions. These values of ϵ were plotted against the *p*H. The *p*H which falls on the curve midway between the horizontal sections was taken as pK_a which was then converted to pK_b by use of the value of pK_w of 14.10 as determined by Miller.[1b] Duplicate determinations were run.

The basic ionization constants of the fluoro- and bromoquinolines are given in Table II. It can be seen that all of the K_b's given for the substituted quinolines are weaker than quinoline itself. This is to be expected if one considers the fact that the halogens are electronegative and by an inductive effect cause a general drain of electrons from the ring. This inductive effect seems to be greater than the donation of electrons to the ring as one would at first be led to believe. This induction is greater the nearer the halogen is to the ring nitrogen. The effect is particularly strong if the halogen is on the pyridinoid ring.

TABLE II

DISSOCIATION CONSTANTS OF SOME QUINOLINES AT 25°

Compound	Dissociation constants
Quinoline[1b]	4.9×10^{-10}
2-Bromoquinoline	$6.0, 6.0, 6.2, 6.2 \times 10^{-14}$
3-Bromoquinoline	$3.1, 3.2, 3.2, 3.4 \times 10^{-12}$
5-Bromoquinoline	$2.2, 2.3, 2.3, 2.4 \times 10^{-11}$
6-Bromoquinoline	$4.4, 4.4, 4.6, 4.6 \times 10^{-11}$
7-Bromoquinoline	$3.9, 4.1, 4.2 \times 10^{-11}$
8-Bromoquinoline	$6.9, 7.2, 7.8, 7.8 \times 10^{-12}$
3-Fluoroquinoline[1b]	2.3×10^{-12}
5-Fluoroquinoline	4.8×10^{-11}
6-Fluoroquinoline	1×10^{-10}
7-Fluoroquinoline	1×10^{-10}
8-Fluoroquinoline	1.2×11^{-11}

By considering the geometry of the molecule it is seen that the inductive effect leaves an *ortho* or *para* position with a smaller electron density than on unsubstituted quinoline. We shall call the positions positive with the understanding that we mean less negative than the same position in quinoline. These positive centers then attract protons less readily than they would otherwise. From calculations of electron densities in quinoline[10] it is seen that the

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(10) H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947).

nitrogen has a much higher electron density than any of the carbon atoms. From the considerations above, a halogen substituted in the 2-position lowers this electron density and gives a low basic dissociation constant. In similar manner a halogen in the 4-position lowers the K_b. However, a halogen in the 3-position would not cause as great an electron decrease and would be stronger than the 2- or 4-compound. The 4-haloquinolines are difficult to prepare and have not been run. Miller[1b] found the 2-fluoroquinoline an extremely weak base that is extensively hydrolyzed in acid solution.

The order of basicity cannot be predicted by electronic resonance forms when the halogen is substituted on the benzenoid ring. The proximity of the halogen to the nitrogen seems to be the predominant factor in these cases. The 5-, 6- and 7-fluoroquinolines as well as the 5-, 6- and 7-bromoquinolines have dissociation constants of nearly the same value. These positions are farthest from the nitrogen and should thus be expected to cause the least influence on the electron density at the nitrogen atom. The 8-haloquinolines have small dissociation constants comparable to the 3-haloquinolines, both being the same distance from the nitrogen.

Experimental

Absorption Spectra.—The spectra were determined with a Beckman quartz spectrophotometer, Model DU, Serial No. 958. The optical densities were measured at intervals of not more than 2 mμ, and at maxima and minima at intervals of 1 mμ. Silica absorption cells were used; the thickness of each was 1.000 ± 0.002 cm. The concentrations varied from 0.00015 to 0.0002 molar. The molecular extinction coefficients, E, were calculated using the equation

$$E = D/lC$$

where

D = optical density defined as $\log_{10} \frac{I_0}{I}$

l = thickness of absorption cell in cm.

C = concn. of sample in moles per liter

Dissociation Constants.—All pH measurements were made with a Leeds and Northrup pH Indicator, Model No. 7664, serial no. 1083347, with glass electrode and saturated calomel reference electrode. Each solution was placed in a constant temperature bath at 25° for at least an hour before measuring pH.

Materials.—The 3-bromoquinoline was Eastman Kodak Co. practical grade product and was redistilled before using. The 2-, 5-, 6-, 7- and 8-bromoquinolines were prepared in this Laboratory.

Solvents. (a) Alcohol.—U.S.P. 190 proof ethyl alcohol, manufactured by U.S. Industrial Chemicals, Inc., was used. The solutions were made 10% ethanol by diluting 12.80 ml. of 95% alcohol to 100 ml. with water.

(b) Acid and Base.—Standard hydrochloric acid and sodium hydroxide solutions were prepared from reagent grade chemicals. The solutions were made 0.01 M in acid by adding the calculated amount of acid to each solution before diluting.

Acknowledgment.—This work was partially supported by the Office of Ordnance Research, U. S. Army, under Contract No. DA-36-034-ORD-1140.

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Formation Constants of Some Metal Complexes of Tropolone and its Derivatives. III. The Benzotropolones and Purpurogallins[1,2]

BY BURL E. BRYANT[3] AND W. CONARD FERNELIUS

RECEIVED MARCH 29, 1954

Formation constants of several metal derivatives of dimethylpurpurogallin, 3,4-benzotropolone and 4,5-benzotropolone have been determined in 50% dioxane. Evidence for the five-membered chelate ring in the complexes of dimethylpurpurogallin is presented. The coördinating ability of the tropolone nucleus has been found to be decreased by the fusion of a benzenoid ring.

In continuation[4,5] of the investigation of the tendency of tropolone and its derivatives to form coördination compounds with metal ions, the behavior of some tropolones with fused benzenoid rings has been studied.

The authors wish to acknowledge gratefully the gift by Professor T. Nozoe of Tohoku University, Sendai, Japan, of the 3,4-benzotropolone used in this study. 4,5-Benzotropolone (m.p. 158°) was prepared by the method of Tarbell and Bill.[6] Purpurogallin was prepared by the method of Evans and Dehn[7] and purified by sublimation: long, red needles m.p. 276° dec.; reported m.p. 276° dec. Dimethylpurpurogallin was prepared from purpurogallin by the method of Haworth, *et al.*,[8] and purified by repeated recrystallization from 95% ethanol; reddish-orange plates, m.p. 152–153°; reported[8] m.p. 156°. *Anal.* Calcd. for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 62.46; H, 4.84 Trimethylpurpurogallin was prepared by the method of Haworth, *et al.*,[8] and purified by repeated crystallization from ethanol: yellow needles m.p. 175–177°; reported 173–175°.

Titrations and calculations of constants were made as described previously.[5] Results are shown in Table I.

Discussion

Unfortunately, purpurogallin did not prove amenable to the method of study employed in this

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[1] Taken in part from a thesis presented by Burl E. Bryant in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1952.

[2] Presented in part before the Fifth annual Meeting-in-Miniature of the Philadelphia Section of the American Chemical Society, January 29, 1953.

[3] Public Health Service Research Fellow of the National Institutes of Health, 1953–1954.

[4] B. E. Bryant, W. C. Fernelius and B. E. Douglas, THIS JOURNAL, **75**, 3784 (1953).

[5] B. E. Bryant and W. C. Fernelius, *ibid.*, **76**, 1696 (1954).

[6] D. S. Tarbell and J. C. Bill, *ibid.*, **74**, 1234 (1952).

[7] T. W. Evans and W. M. Dehn, *ibid.*, **52**, 3647 (1930).

[8] R. D. Haworth, B. P. Moore and P. T. Pauson, *J. Chem. Soc.*, 1045 (1948).