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 *p*H measurements were made with a Leeds and Northrup *p*H 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 *p*H.

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.

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[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

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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).

TABLE I

FORMATION CONSTANTS, K_n, FOR METAL DERIVATIVES OR BENZOTROPOLONES MEASURED IN 50–50 DIOXANE–WATER AT 30°

	log K_n	H^+	Cu^{++}	Be^{++}	Pb^{++}	Zn^+	Ni^{++}	Co^{++}	Mg^{++}	Ca^{++}
Dimethylpurpurogallin	$n = 1$	9.76	9.2	k_{av}	[b]	6.8	6.7	6.6	4.9	4.5
	$n = 2$		7.4	8		5.7	5.1	5.2	3.9	3.5
	$n = 3$						2.8	3.1		
4,5-Benzotropolone	$n = 1$	10.2	[a]	8.8	8.8	[c]	7.8	ppt.		
	$n = 2$			7.4	6.4		6.2			
3,4-Benzotropolone	$n = 1$	10.4	10.8	9.2			7.8			
	$n = 2$		8.9	7.9			6.3			
	$n = 3$						3.7			

[a] Yellow green ppt. [b] Soln. becomes very dark and turbid. [c] Yellow ppt. m. >300°.

investigation. The multiplicity of dissociable protons makes an accurate determination of acid dissociation constants very difficult. No break in the titration curve was detectable after the addition of two equivalents of base. In basic solution purpurogallin was found to undergo an irreversible color change.

Potentiometric titrations showed that dimethylpurpurogallin behaves as a monobasic acid, while the trimethyl ether is not noticeably acidic. This conduct may be related to that of the methylation of purpurogallin where the trimethyl ether may be obtained using diazomethane whereas the preparation of the tetramethyl ether requires dimethyl sulfate in basic solution.

Thorn and Barclay[9] investigated the ultraviolet spectra of purpurogallin and its methyl ethers. Their results also indicate that the fourth proton of purpurogallin is appreciably different from the other three. All this evidence points to the existence of a very stable hydrogen bond between the carbonyl group and the adjacent hydroxyl of the benzenoid ring.

The behavior of the methyl ethers in the presence of metal ions capable of coördination suggests that coördination proceeds by formation of a five-membered chelate ring containing the metal ion. Trimethylpurpurogallin shows no measurable interaction under these conditions with the metals studied. Dimethylpurpurogallin behaves as a monobasic acid even in the presence of metal ions with which it forms stable complexes. The reaction of metal ions with dimethylpurpurogallin suggests that the hydrogen bond is not ruptured when the metal derivatives are formed since the metal complexes do not exhibit the acidity expected for a phenolic compound. If these metal derivatives are chelate compounds, the carbonyl oxygen must be interacting with both the proton and the metal ion. This view receives support from the observations of Simpson and Gorden.[10] These workers report evidence for simultaneous interaction of a single carbonyl group with two hydroxyl hydrogens in a flavonol.

The stability of none of the complexes formed by the compounds reported in this paper is as great as that of a complex of an alkyltropolone of the same pK_D. It should be noted that the difference in stability of the complexes of the benzotropolones on the one hand and those of dimethylpurpurogallin on the other is greater than would be predicted on the basis of their acid dissociation constants. The earlier work of Calvin and Wilson[11] demonstrated that the fusion of a resonating ring system to the chelate ring considerably decreased the stability of the chelate ring. This phenomenon may be thought of as an "interference" with the resonance of the chelate ring. This explanation appears to be applicable to the three chelating agents reported here, but is not sufficient to explain the unusually low stabilities of the complexes of dimethylpurpurogallin.

If the suggestion that the six-membered ring formed by hydrogen bonding in the dimethylpurpurogallin molecule remains intact in the metal complexes is correct, a relatively low stability of the metal chelate would be predicted. The reason for this prediction is, of course, that the electron cloud around the oxygen is distorted by the proton. It must be assumed that the metal ion finds the electron availability on the carbonyl oxygen appreciably lower in the dimethylpurpurogallin than in the benzotropolones. An investigation of these concepts as applied to other compounds is under way.

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[10] T. H. Simpson and T. Gorden, *J. Chem. Soc.*, 4638 (1952).

[11] M. Calvin and K. Wilson, THIS JOURNAL, **67**, 2003 (1945).