

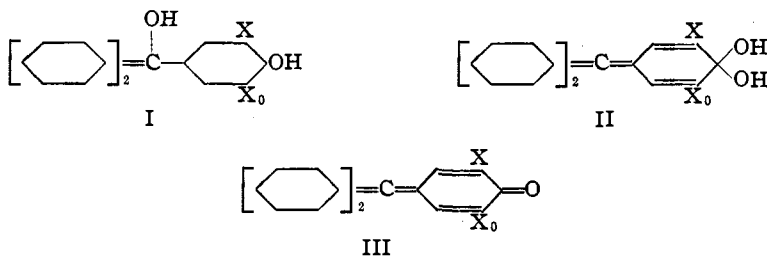
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

TAUTOMERISM OF HYDROXYTRIARYLCARBINOLS. III¹BY LEIGH C. ANDERSON AND M. B. GEIGER¹

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Previous papers from this Laboratory² have shown that a marked change in absorption spectra occurs on changing from the colorless benzenoid *p*-hydroxytriphenylcarbinols to the corresponding colored carbinols. These spectroscopic data were interpreted as constituting further evidence for the existence of a quinonoid tautomer (II) of the corresponding benzenoid carbinol (I). The fact that the colorless carbinol possesses a benzenoid structure has not been doubted, and the structure of the corresponding fuchsonone (III) has never been called in question. Explanations for the



existence of the colored carbinol, however, have implied the suggestion that it is a hydrate of the fuchsonone,³ or that it is a mixture of the benzenoid carbinol with small amounts of the highly colored fuchsonone as impurity. Chemical evidence by Gomberg and co-workers⁴ has definitely shown that the colored carbinol is not an impure benzenoid carbinol.

This work was undertaken in order to obtain further data concerning this class of compounds with the hope that certain effects that were observed in previous work in regard to the position and height of the absorption bands might now be explained.

¹ The material in this and the succeeding paper comprises a portion of a thesis presented by M. B. Geiger to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1931.

² (a) Anderson and Gomberg, *THIS JOURNAL*, **50**, 203 (1928); (b) Anderson, *ibid.*, **51**, 1889 (1929).

³ (a) Auwers and Schröter, *Ber.*, **36**, 3247 (1903); (b) Orndorff, Gibbs, McNulty and Shapiro, *THIS JOURNAL*, **49**, 1546 (1927). In the latter article the statement is made that "Gomberg has shown that fuchsonone readily takes up water to form the quinoid hydrate." The word hydrate in this connection is ambiguous and was not used by Gomberg. He states in the article from which the above inference was drawn [*THIS JOURNAL*, **35**, 1037 (1913)] "nor does either of the two molecules contain water of crystallization."

⁴ Gomberg, *THIS JOURNAL*, **35**, 1035 (1913); Gomberg and Van Stone, *ibid.*, **38**, 1577 (1916).

In Figs. 1, 2, 3 and 4, respectively, are given the curves for the quantitative spectra of the methane, colorless carbinol (except for the 3-chloro-), colored carbinol, and the fuchsons of each of the following: 3-chloro-4-hydroxy-, 3-bromo-4-hydroxy-, 3,5-dichloro-4-hydroxy- and 3,5-dibromo-4-hydroxy-triphenylcarbinol. The methanes and colorless carbinols are undoubtedly benzenoid in constitution while the fuchsons contain a quinonoid nucleus.

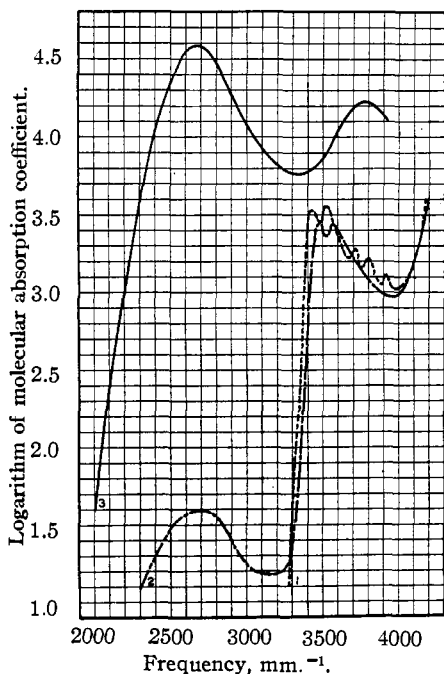


Fig. 1.—3-Chloro-4-hydroxytriphenylcarbinol: 1, methane; 2, carbinol, colored; 3, fuchson.

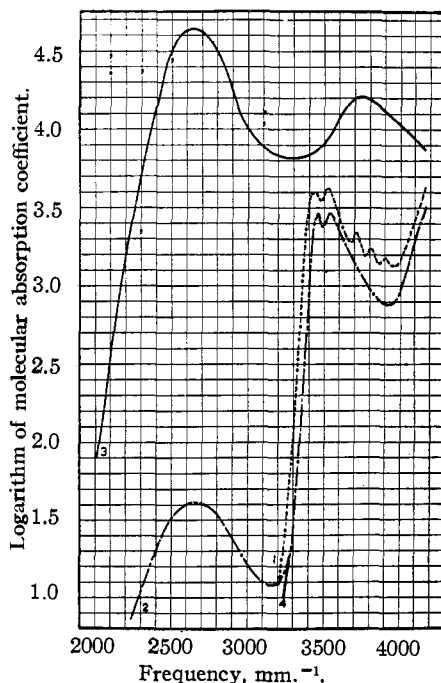


Fig. 2.—3-Bromo-4-hydroxytriphenylcarbinol: 1, methane; 2, carbinol, colored; 3, fuchson; 4, carbinol, colorless.

The similarity of the curves for the corresponding derivatives in each of the groups is very striking. All of the fuchsons have an intense absorption band on the edge of the visible region of the spectrum and another band in the ultraviolet. The methanes have no absorption in the visible region but have a series of bands in the ultraviolet between frequencies 3400 and 4000 mm.^{-1} . The benzenoid carbinols show no absorption in the visible region of the spectrum, and their ultraviolet absorption consists of a number of fine bands very similar to those of the methanes. The colored carbinols have spectra resembling both the fuchsons and the benzenoid carbinols in that they have an absorption band in the visible region of the spectrum and the ultraviolet absorption is practically identical with the ultraviolet absorption of the colorless carbinol.

The progressive substitution of one chlorine atom, one bromine atom, two chlorine atoms and two bromine atoms for the hydrogens in the ortho positions to the nuclear hydroxyl group in the 4-hydroxytriphenylcarbinol compounds causes a shift in the intense absorption band for the fuchsones toward the longer wave lengths. A similar change is noted for the band in the visible for the colored carbinols and for the two most persistent bands in the ultraviolet for the methanes, colorless carbinols and colored carbinols.

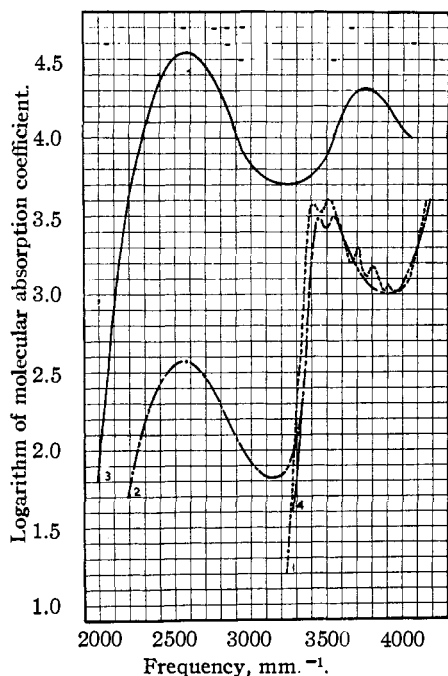


Fig. 3.—3,5-dichloro-4-hydroxytriphenylcarbinol: 1, methane; 2, carbinol, colored; 3, fuchson; 4, carbinol, colorless.

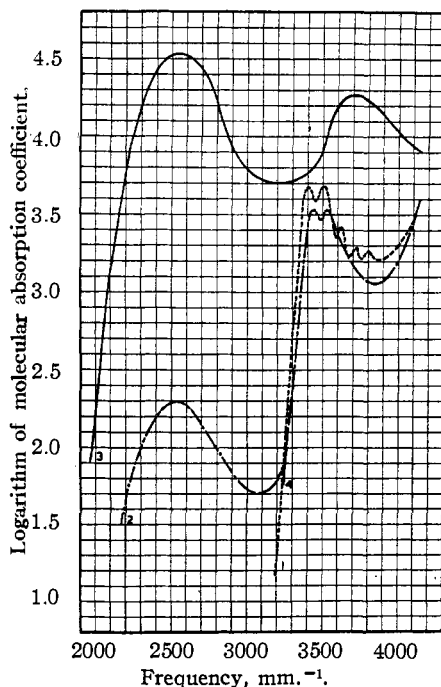


Fig. 4.—3,5-Dibromo-4-hydroxytriphenylcarbinol: 1, methane; 2, carbinol, colored; 3, fuchson; 4, carbinol, colorless.

The height of the quinonoid band⁵ for the various fuchsones is approximately the same. In all cases which have been observed the quinonoid band for the colored carbinols is much lower than the quinonoid band for the fuchsones; Table I lists the heights of the quinonoid bands of the fuchsones and the colored carbinols expressed as logarithms of the molecular absorption coefficients. If the colored carbinol were a hydrate of the corresponding fuchson such a variation would not be expected. The curve for the hydrate calculated on the basis of fuchson should be 93.5%

⁵ The band which occurs in the edge of the visible and near ultraviolet in the spectra of these fuchsones and colored carbinols will be called, for convenience of description, the quinonoid band.

TABLE I
HEIGHTS OF THE QUINONOID BANDS

3-X,5-X ₀ ,4-hydroxy- triphenylcarbinol	a		b		c		d		e	
	X H	X ₀ H	X H	X ₀ Cl	X H	X ₀ Br	X Cl	X ₀ Cl	X Br	X ₀ Br
Fuchsones	4.48		4.58		4.64		4.54		4.53	
Colored carbinols	2.52		1.59		1.61		2.57		2.30	

as high as the curve for the fuchsones. The difference which has been found in the height of the bands is, therefore, much more than would be accounted for by the effect of a molecule of water in so heavy a molecule as the fuchsones, even assuming that it were a hydrate and that it would all remain hydrated in so dilute an ether solution.

It has been found that the colored carbinols with symmetrical substitution in the nucleus (a, d, e, Table I) have quinonoid bands whose heights are of the same order of magnitude. The height of the quinonoid bands for the colored carbinols with unsymmetrical substitution (b and c, Table I) is even lower than the band for those with symmetrical substitution, but when compared with each other, they are of the same order of magnitude.

Figure 5 gives the position of the peaks or frequencies of maximum absorption of the bands for the colored carbinols (Q) and the fuchsones (F) of the different carbinols studied in this investigation and also includes those described in the papers previously referred to. It will be noted that in the case of some of the carbinols the frequency of maximum absorption of the quinonoid band for the colored carbinol as compared to the frequency of maximum absorption of the quinonoid band for the corresponding fuchsones is shifted toward the shorter wave lengths while in other cases it is shifted toward the longer wave lengths. The displacement of the peaks for the colored carbinols and the corresponding fuchsones is greater than the experimental error of determining the position of these peaks for the compounds indicated as a, c, d, f, g, h and i while for b and e the displacement is less than the experimental error. In a, h and i the peak for the fuchsones compared to that of the corresponding carbinol is displaced toward the shorter wave lengths, while in all the other groups the displacement is toward the longer wave lengths. These data allow an interesting observation to be made. When the groups in the ortho position to the nuclear hydroxyl are the same (a, h and i) the displacement of the peak for the quinonoid band of the colored carbinol compared to that of the fuchsones is toward the longer wave lengths. If the groups in the ortho position to the nuclear hydroxyl are not alike, then the displacement is in the opposite sense. It does not seem likely that this relation is due to chance, since no inconsistencies have been observed in any of the compounds studied.

The fact that the position of the quinonoid band for the colored carbinol and the quinonoid band for the corresponding fuchsones is not at the same

frequency is a positive indication that the colored carbinol is not the colorless carbinol with small amounts of fuchsone as impurity. The two effects, namely, the displacement of the quinonoid band for the colored carbinol as compared to that of the fuchsone and the lowering of the quinonoid absorption band of the colored form of 4-hydroxytriphenylcarbinol by a

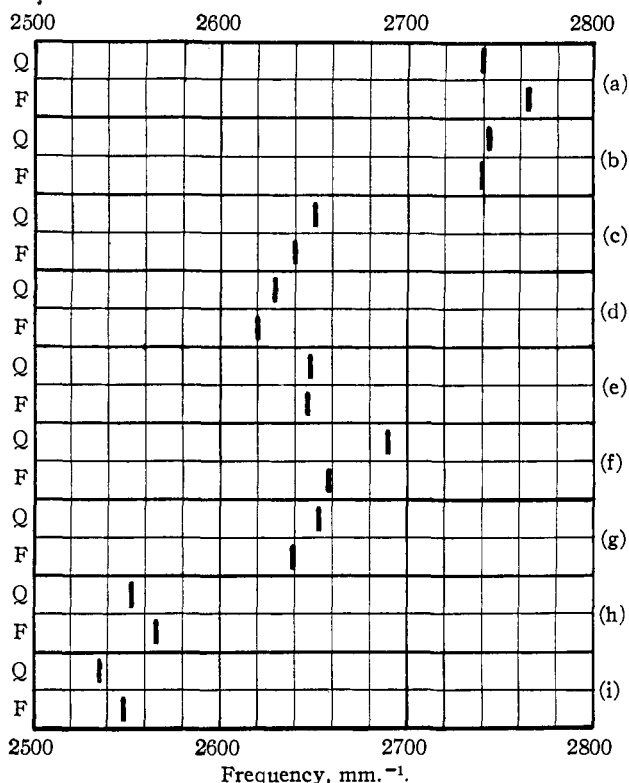


Fig. 5.—Q = colored carbinol; F = fuchsone: (a) 4-hydroxytriphenylcarbinol; (b) 3-methyl-4-hydroxytriphenylcarbinol; (c) 3-methyl-5-chloro-4-hydroxytriphenylcarbinol; (d) 3-methyl-5-bromo-4-hydroxytriphenylcarbinol; (e) 3-methoxy-4-hydroxytriphenylcarbinol; (f) 3-chloro-4-hydroxytriphenylcarbinol; (g) 3-bromo-4-hydroxytriphenylcarbinol; (h) 3,5-dichloro-4-hydroxytriphenylcarbinol; (i) 3,5-dibromo-4-hydroxytriphenylcarbinol.

definite amount, both of which phenomena occur when one and two of the hydrogens adjacent to the nuclear hydroxyl group are replaced, appear to be evidence in favor of the hypothesis that the ring in which the substitution has been made has a very direct influence upon the nature of the electron transition which produces this band and also upon the probability of the occurrence of this transition.

TABLE II
FREQUENCY NUMBERS OF BANDS IN ETHER SOLUTIONS

	3-Cl-4-OH triphenyl	3-Br-4-OH triphenyl	3,5,Cl ₂ -4-OH triphenyl	3,5-Br ₂ -4-OH triphenyl
Methane	3449	3433	3414	3409
	3530	3516	3508	3502
	3704	3702	3700	3702
	3802	3802	3802	3804
	3901	3906	3897	3906
	4014			
Carbinol (colorless)		3463	3445	3436
		3548	3550	3532
		3715	3654	3633
		3770	3717	3715
		3865	3771	3770
		3960	3865	3866
Carbinol (colored)			3963	3963
	2690	2654	2552	2540
	3477	3463	3445	3430
	3558	3549	3547	3520
	3720	3644	3658	3639
	3771	3718	3720	3715
	3862	3770	3783	3786
	3958	3859	3864	3865
		3949	3956	3956
	Carbinol fuchstone	2659	2639	2567
3713		3720	3701	3668

Experimental

The apparatus and the methods used for obtaining the quantitative absorption spectra as well as the methods employed for determining the frequencies of maximum absorption have been described.²

The four fuchstones studied in this investigation were each prepared according to the method of Gomberg and Van Stone.⁴ They were all carefully crystallized from ether which showed no selective absorption between 2300 and 7500 Å. The four colored carbinols were prepared by adding hot water to a solution of the corresponding fuchstone in glacial acetic acid until the concentration of the acetic acid in the solution had been reduced to 60%. After allowing the mixture to cool the crystals were filtered off and dried in a vacuum desiccator over soda lime. Each of the three colorless carbinols was prepared by dissolving the corresponding fuchstone in normal alkali and treating the clear, cold solution with ammonium chloride. The precipitate was filtered off and crystallized from optically clear ether and hexane. The four methanes that were studied were prepared by reducing the corresponding fuchstone with zinc dust and glacial acetic acid. Each of them was crystallized from optically clear hexane. The melting points of the compounds prepared as described above are as follows (degrees centigrade):

	Methane	Carbinol		Fuchstone
		Colorless	Colored	
3-Chloro-4-hydroxytriphenyl	73		124-125	161
3-Bromo-4-hydroxytriphenyl	79	108.5-109	105-105.5	139.5
3,5-Dichloro-4-hydroxytriphenyl	105	132	133-134	216
3,5-Dibromo-4-hydroxytriphenyl	130	136	136-137	233

Summary

1. Curves have been prepared which show the quantitative absorption spectra of the methane, colored carbinol and fuchsons of each of the following compounds: 3-chloro-4-hydroxytriphenylcarbinol, 3-bromo-4-hydroxytriphenylcarbinol, 3,5-dichloro-4-hydroxytriphenylcarbinol and 3,5-dibromo-4-hydroxytriphenylcarbinol together with the curves for the colorless carbinols of the last three compounds.

2. Symmetrical or unsymmetrical substitution in the ortho positions to the nuclear hydroxyl group of 4-hydroxytriphenylcarbinol has been shown to have a definite effect upon the height of the quinonoid band for the colored carbinol; symmetrical substitution producing a greater absorption.

3. The direction of the displacement of the quinonoid band for the colored carbinol, in reference to the position for the quinonoid band for the corresponding fuchsons of the 4-hydroxytriphenylcarbinol series has also been found to be dependent upon the groups substituted in the ortho positions to the nuclear hydroxyl. If the two groups are the same the displacement is in one direction, while if they are different, the displacement is in the opposite direction.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

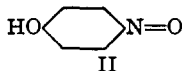
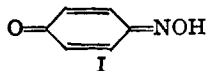
THE TAUTOMERISM OF QUINONEOXIME AND *PARA*-NITROSOPHENOL

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The chemical reactions and the methods of preparation of quinoneoxime (I) indicate that it is in tautomeric equilibrium with *p*-nitrosophenol (II); the relative amounts of the two substances present being dependent upon the solvent and conditions which are employed.



It has been generally accepted that the methyl ethers of tautomeric substances do not undergo tautomerization and that in many instances each can be obtained pure. A comparison of the physical properties of a solution of the tautomeric mixture of non-methylated substances with solutions of each of the corresponding methyl ether isomers has been used in investigations of compounds such as isatin, acetoacetic ester, etc., to determine the extent to which each of the tautomeric forms occurs in the equilibrium mixture. This procedure has been followed in the present investigation in the case of the mixture of quinoneoxime and *p*-nitrosophenol. Ether has been chosen as the solvent because it is optically