[CONTRIBUTION FROM THE THOMPSON CHEMICAL LABORATORY, WILLIAMS COLLEGE]

# THE ABSORPTION SPECTRA OF SOME SUBSTITUTED QUINOLINES AND THEIR METHIODIDES[1]

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The present paper brings together for comparison the absorption spectra of a group of quinoline derivatives: quinaldine, lepidine, the 2- and 4-styrylquinolines, and 2-(4-phenyl-1,3-butadienyl)quinoline, together with the methiodides of these compounds. For comparison the spectra of quinoline and quinoline methiodide are included. The data are summarized in Table I, and there are brought together in Figures 1 and 2 representative absorption spectrum curves.

## EXPERIMENTAL

All melting points are corrected.

The *quinoline* and *quinaldine* used were Eastman White Label grade twice distilled through a ten-inch column at 3–8 mm. pressure. The *lepidine* was Reilly technical grade twice distilled similarly at 3–8 mm. pressure.

*Quinoline, quinaldine, and lepidine methiodides.* Equal molecular amounts of methyl iodide and the base were mixed in a small amount of absolute methanol and refluxed for 20 hours. Recrystallizations were from absolute methanol; melting points: quinoline methiodide, 131–132° [reported 133° (3)], quinaldine methiodide, 195–196° [reported 195° (3)], lepidine methiodide, 174–175° [reported 173–174° (3)].

*2-Styrylquinoline.* This compound was prepared by the procedure of Pfeiffer, *et al.* (4) as modified by Compton and Bergmann (2). It melted at 98–99° (reported 98.4–98.6°).

*2-(4-Phenyl-1,3-butadienyl)quinoline.* This compound was prepared by the procedure of Compton and Bergmann (2). It melted at 117–117.5° (reported 117.2–117.4°).

*4-Styrylquinoline.* This compound was prepared by the procedure of Ainley and King (5) with minor modifications. It melted at 98–99° (no melting point previously reported).

*Anal.* Calc'd for $C_{17}H_{13}N$: N, 6.05. Found: N, 6.36, 6.19.

*2-Styrylquinoline methiodide.* A mixture of 20 g. (0.086 mole) of 2-stryylquinoline and 15.4 g. (0.109 mole) of methyl iodide were refluxed on a water-bath for 3 hours. Three recrystallizations from 95% ethanol, including a treatment with decolorizing carbon, gave 7.3 g. (22%) of bright yellow needles, m.p. 225–227°. [M.p. reported by Werner (6), 235.2° d.].

*Anal.* Calc'd for $C_{18}H_{16}IN$: I, 34.01. Found: I, 34.02, 33.75.

*4-Styrylquinoline methiodide.* A mixture of 110 g. (0.40 mole) of 4-methylquinoline methiodide and 45 g. (0.34 mole) of freshly distilled benzaldehyde was dissolved in 550 ml. of absolute ethanol. Then 2.5 ml. of piperidine was added and the solution was refluxed for 5 hours and then cooled overnight. A gummy solid was isolated and digested with ether, benzene, and ligroin. Five recrystallizations from methanol and water gave 39.2 g. (26%) of yellow crystals, m.p. 239–241°.

*Anal.* Calc'd for $C_{18}H_{16}IN$: I, 34.01. Found: I, 34.12, 33.84.

*2-(4-Phenyl-1,3-butadienyl)quinoline methiodide.* A mixture of 13.6 g. (0.053 mole) of 2-(4-phenyl-1,3-butadienyl)quinoline and 13.2 g. (0.09 mole) of methyl iodide was refluxed in 10 ml. of absolute ethanol for 36 hours. Three recrystallizations of the crude product from 25% methanol, including a treatment with decolorizing carbon, gave 5.4 g. (25%) of bright orange needles, m.p. 214.5–215.0°.

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*Anal.* Calc'd for $C_{20}H_{18}IN$: I, 31.78. Found: I, 31.96, 32.22.

*Absorption spectra.* The absorption spectra measurements were made in absolute methanol solution at 25°, using a Model DU Beckman spectrophotometer. Concentrations were of the order of $10^{-5}$ M. Measurements were made every 10 mμ, except in critical regions where measurements were made as close as 1 mμ.

The iodine analyses were made by Tiedcke Laboratories.

TABLE I

Absorption Spectra Data of Some Quinoline Derivatives Measured in Absolute Methanol at Room Temperature

| COMPOUND | COLOR | PRINCIPAL ABSORPTION MAXIMA | |
|---|---|---|---|
| | | $\lambda m\mu$ | log $\epsilon$ |
| Quinoline | Colorless | 276[a] | 3.65 |
| | | 311[a] | 3.8 |
| Quinaldine | Colorless | 274 | 3.54 |
| | | 315 | 3.60 |
| Lepidine | Colorless | 279 | 3.67 |
| | | 313 | 3.43 |
| Quinoline methiodide | Yellow | 316 | 3.88 |
| Quinaldine methiodide | Greenish yellow | 318 | 4.00 |
| Lepidine methiodide | Yellow | 314 | 3.90 |
| 2-Styrylquinoline | Colorless | 283[b] | 4.39 |
| | | 328[c] | 4.35 |
| 4-Styrylquinoline | Colorless | 235 | 4.39 |
| | | 330 | 4.35 |
| 2-(4-Phenyl-1,3-butadienyl)quinoline | Greenish yellow | 296[d] | 4.35 |
| | | 355 | 4.59 |
| 2-Styrylquinoline methiodide | Yellow | 298 | 4.10 |
| | | 375 | 4.48 |
| 4-Styrylquinoline methiodide | Yellow | 317 | 3.95 |
| | | 391 | 3.97 |
| 2-(4-Phenyl-1,3-butadienyl)quinoline methiodide | Orange | 370 | 4.33 |
| | | 412 | 4.42 |

[a] Data of Morton and deGouveia (1) in ethanol. [b] Previously reported by Compton and Bergmann (2): 281 and 320 mμ in chloroform. [c] Estimated from broad peak. [d] Previously reported by Compton and Bergmann (2): 296 and 358 mμ in chloroform.

## DISCUSSION

The lack of any significant difference among the spectra of quinoline, quinaldine, and lepidine is what would be expected on the basis of the electronic oscillation concept of Lewis and Calvin (7). The presence of the methyl groups on the quinoline nucleus should not alter materially the nature of those polar structures most directly related to the absorption characteristics. The conversion of each of these bases to a methiodide brings about a displacement of the principal absorption peak towards a longer wavelength. This also would be expected since the presence of the positive charge in the quinolinium ion makes possible polar structures involving shifts in the position of this positive charge. Such ionic structures are not possible in the free bases. The similarity in the spectra of the methiodides of quinoline, quinaldine, and lepidine would be expected since, as in the cases of the bases themselves, the presence of the methyl groups on the quinolinium nucleus should not alter materially the nature of the important polar forms. The wavelength shifts towards longer wavelengths accompanying substitution by styryl and 4-phenyl-1,3-butadienyl groups in the 2-position have been considered previously (2).

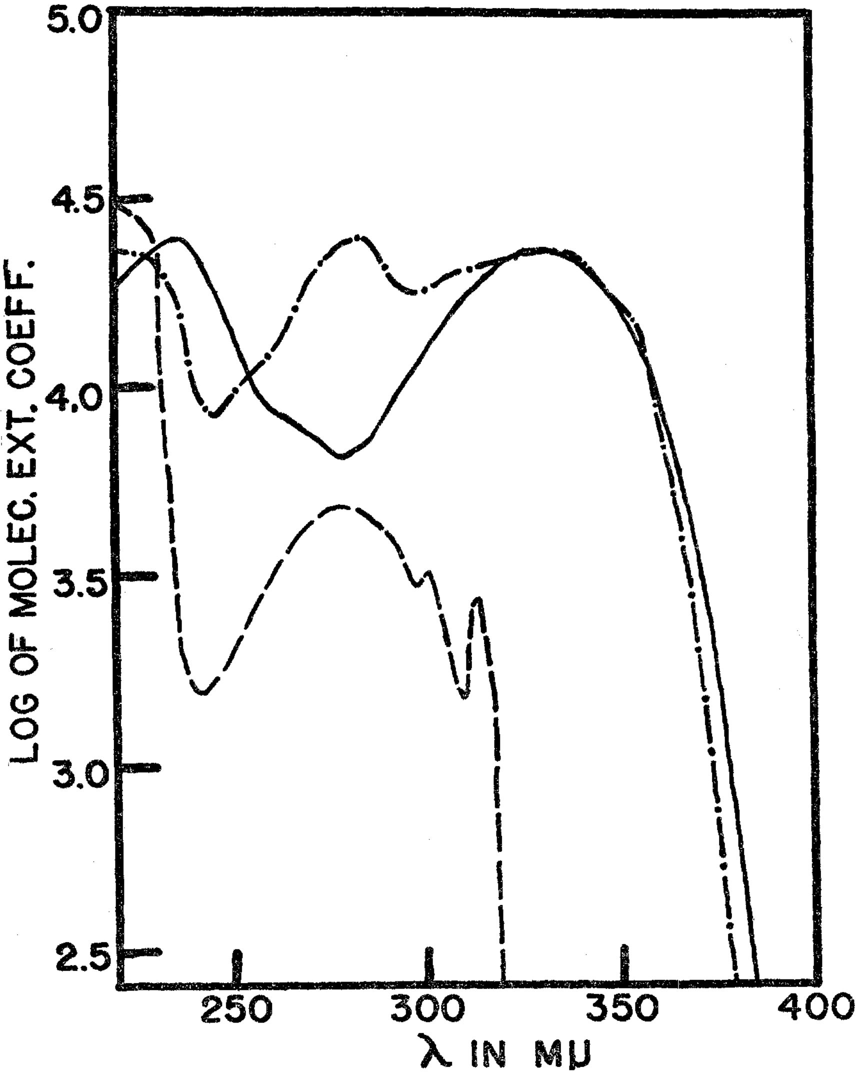


FIG. 1. ABSORPTION SPECTRA OF LEPIDINE (— —), 2-STYRYLQUINOLINE (————), AND 4-STYRYLQUINOLINE (—•—) IN ABSOLUTE METHANOL AT ROOM TEMPERATURE

Shifts of principal absorption peaks towards longer wavelengths are observed to accompany the conversion of the 2-styryl, the 4-styryl, and the 4-phenyl-1,3-butadienyl compounds to their methiodides. Such shifts would be expected since in each case the presence of the positive charge in the substituted quinolinium ion makes possible polar structures such as I and II. Such ionic structures are not possible in the corresponding styrylquinolines.

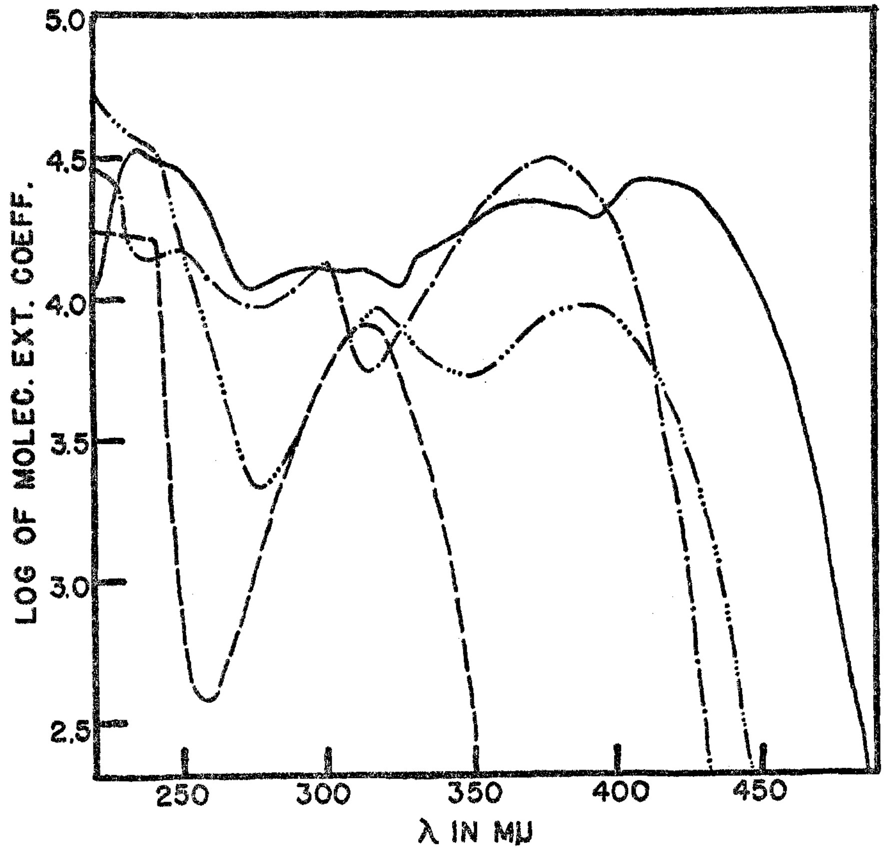
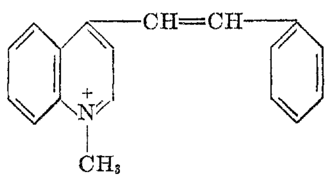
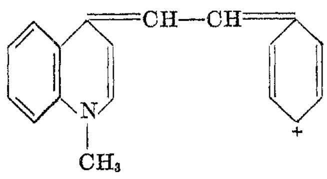


Fig. 2. Absorption Spectra of Lepidine Methiodide (- -), 2-Styrylquinoline Methiodide (-•-), 4-Styrylquinoline Methiodide (-•••), and 2-(4-Phenyl-1,3-butadienyl)quinoline Methiodide (————) in Absolute Methanol at Room Temperature

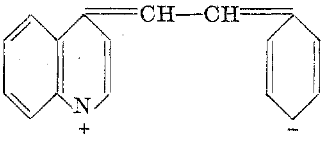


I

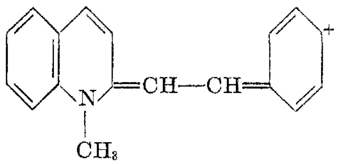


II

It is of interest that substitution of styryl and 4-phenyl-1,3-butadienyl groups in the 2-position of quinoline brings about shifts of about 52 mμ and 79 mμ respectively, whereas corresponding substitution on the 2-position of quinoline methiodide brings about shifts of about 59 mμ and 96 mμ respectively. All of these wavelength shifts are probably due to the increase in the chain of double bonds in the mobile electronic system brought about by the substitution. This extension would probably have a greater effect in the case of the substituted quinoline methiodides since polar structures such as II would be expected to be more easily achieved than polar structures of the substituted quinolines, such as III.



III



IV

It is to be noted also that substitution of a styryl group in the 4-position of quinoline brings about a wavelength shift of the principal maximum not significantly different than the shift brought about by styryl substitution in the 2-position. Substitution of a styryl group in the 4-position of quinoline methiodide, however, brings about a shift greater by about 16 mμ than the shift resulting from styryl substitution in the 2-position. This greater effect of the position of substitution in the case of quinoline methiodide is probably associated with the longer chain of double bonds in the mobile electronic system for 4-styrylquinoline methiodide indicated by structures such as II, as compared with the double bond chain for 2-styrylquinoline methiodide indicated by the corresponding structures, such as IV.

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## SUMMARY

A comparison has been made of the absorption spectra of a group of substituted quinolines and their methiodides. It has been shown that, for the cases studied, substitution by styryl and 4-phenyl-1,3-butadienyl groups has a greater effect in the case of quinoline methiodide than it has in the case of quinoline.

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## REFERENCES

(1) MORTON AND DE GOUVEIA, *J. Chem. Soc.*, 916 (1934).
(2) COMPTON AND BERGMANN, *J. Org. Chem.*, **12**, 363 (1947).
(3) HEILBRON, *Dictionary of Organic Compounds*, Oxford, New York, 1936.
(4) PFEIFFER, RHEINBOLT, AND WOLF, *Ann.*, **441**, 265 (1925).
(5) AINLEY AND KING, *Proc. Roy. Soc. (London)*, **B125**, 60 (1938).
(6) WERNER, *J. Am. Chem. Soc.*, **42**, 2309 (1920).
(7) LEWIS AND CALVIN, *Chem. Revs.*, **25**, 273 (1939).