[Contribution from the Sterling Chemistry Laboratory, Yale University]

THE PREPARATION AND ABSORPTION SPECTRA OF α-(α-QUINOLYL)-ω-PHENYLPOLYENES[1]

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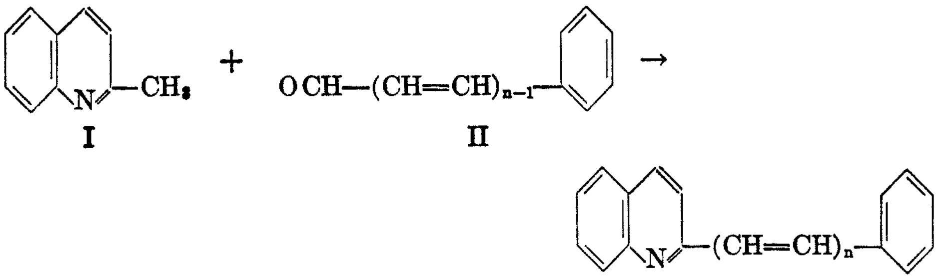
The classical studies by Kuhn and Winterstein (1) on the synthesis and the chemical and the physical properties of diphenylpolyenes have not only materially assisted in the elucidation of the structure of carotenoids, but have also provided significant examples illustrating the relations which exist between the color and constitution of organic compounds. The present paper deals with an extension of such studies to a series of heterocyclic polyenes which differ from the diphenylpolyenes solely in the replacement of one terminal phenyl group by the α-quinolyl group. The first two members of this series (III, n = 1, 2) have been known for some time. Their preparation was first accomplished by Wallach (2) and Renz (3) through the condensation of quinaldine (I) with benzaldehyde (II, n = 1) or cinnamaldehyde (II, n = 2).



I

II

III. α-(α-Quinolyl)-ω-phenylpolyene

This general method has more recently been modified by Pfeiffer (4) and Spaeth (5). The phenylpolyenals necessary for an extension of this series have recently become more readily available through the elegant method described by Schmitt (6). Their condensation with quinaldine was carried out by heating the reagents with zinc chloride to about 100°, a procedure which combines certain features of the methods of Renz (3) and Spaeth (5). With the higher aldehydes, a large excess of quinaldine was required to dissolve the phenylpolyenal. For a direct comparison of the heterocyclic polyenes with the diphenylpolyenes, the latter were prepared according to the method of Kuhn and Winterstein (1).

As shown in Table I the colors of the quinolylphenylpolyenes present the same gradation as those of the diphenylpolyenes. In the heterocyclic series the first colored compound is the butadiene and its color shows a striking similarity to that of the diphenylhexatriene, the first colored compound of the diphenylpolyene

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series. The similarity of color between $C_9H_6N-(CH{=}CH)_n-C_6H_5$ and $C_6H_5-(CH{=}CH)_{n+1}-C_6H_5$ is even more pronounced among the higher vinylogs of the two respective series. On the basis of visual evidence it appears therefore, that the chromophoric character of the α-quinolyl group is equivalent to that of a styryl group.

TABLE I

Comparison of Diphenyl- and α-Quinolyl-ω-phenyl-polyenes

n	$C_6H_5-(CH{=}CH)_n-C_6H_5$		$C_9H_6N-(CH{=}CH)_n-C_6H_5$	
	m.p. °C.	color	m.p. °C.	color
1	124	Colorless	98	Colorless
2	153	Colorless	117	Greenish-yellow
3	200	Greenish-yellow	160	Golden-yellow
4	232	Golden-yellow	195	Orange
5	253	Orange	—	—
6	267	Brown-orange	232	Copper-bronze
7	279	Copper-bronze	—	—

TABLE II

Absorption Maxima in Chloroform at 25°C

COMPOUND	λ max (mμ)		
	(a)	(b)*	(c)
Diphenylethylene	296	310	—
Diphenylbutadiene	319	333	350
Diphenylhexatriene	340	355	374
Diphenyloctatetraene	360	377	403
Diphenyldecapentaene	380	400	425
Diphenyldodecahexaene	396	420	444
Diphenyltetradecaheptaene	413	437	463
Quinolylphenylethylene	281	320	—
Quinolylphenylbutadiene	296	358	—
Quinolylphenylhexatriene	312	377	—
Quinolylphenyloctatetraene	—	398	—
Quinolylphenyldodecahexaene	—	435	457

* The (b) maximum is the most intense in each case except for diphenylethylene and phenylquinolylethylene in which cases the (a) maximum is the most intense.

This is also borne out by a comparison of the absorption spectra of the members of the two series, which were measured in a chloroform solution at 25°. Table II records the wave lengths of the absorption maxima of both series, and Figure 1 shows the spectra of the members of the heterocyclic series. These spectra, like those of the diphenyl series, show the typical increase of absorption intensity and curve character with the lengthening of the exocyclic chain.

Table III presents a comparison of the highest maxima of the various members of the heterocyclic- and diphenyl-polyene series. With the exception of the first member, the maximum of $C_9H_6N—(CH═CH)_n—C_6H_5$ lies practically at the same wave length as that of $C_6H_5—(CH═CH)_{n+1}—C_6H_5$. This relationship is also illustrated by Figure 2 which shows the striking similarity between the absorption spectra of 1-(α-quinolyl)-12-phenyldodecahexaene-1,3,5,7,9,11 and 1,14-diphenyltetradecaheptaene-1,3,5,7,9,11,13.

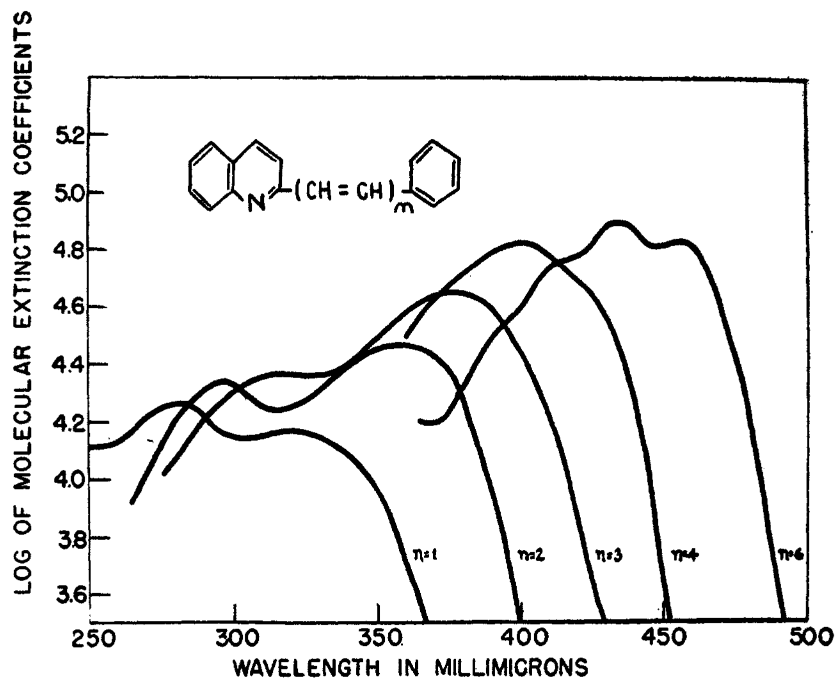

FIG. 1. Absorption curves of α-(α-quinolyl)-ω-phenylpolyenes in chloroform at 25°C.

TABLE III

COMPARISON OF ABSORPTION MAXIMA OF QUINOLYLPHENYL- AND DIPHENYL-POLYENES

	max. (mμ) of $C_9H_6N—(CH═CH)_n—C_6H_5$			
n = 1	2	3	4	6
320	358	377	398	435
333	355	377	400	437
n = 2	3	4	5	7
	max. (mμ) of $C_6H_5—(CH═CH)_n—C_6H_5$			

On the basis of the electronic oscillation concept, Lewis and Calvin (7) have formulated the equation $\lambda^2 = kn$, which relates λ, the wave length of the absorption maximum, to n, the number of double bonds in the exocyclic chain. The data for the diphenylpolyene series, particularly those of the higher members, are in excellent agreement with this relationship. As shown by Figure 3, the same relationship also exists in the α-(α-quinolyl)-ω-phenylpolyene series.

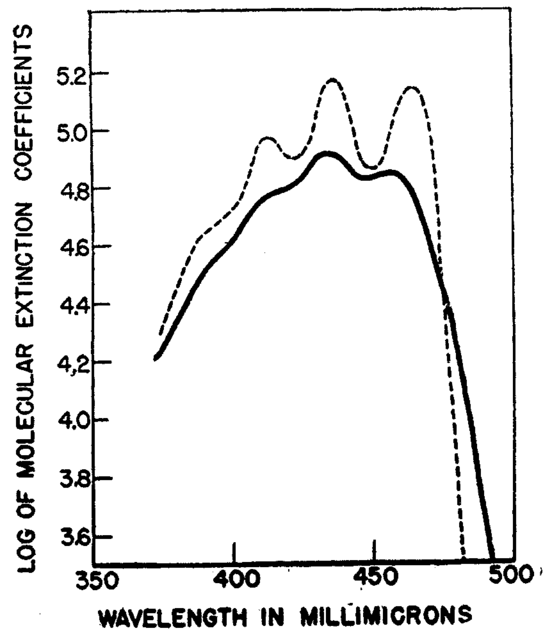

FIG. 2. Absorption spectra of 1-(α-quinolyl)-12-phenyldodecahexaene (solid line) and 1,14-diphenyltetradecaheptaene (broken line) in chloroform at 25°C.

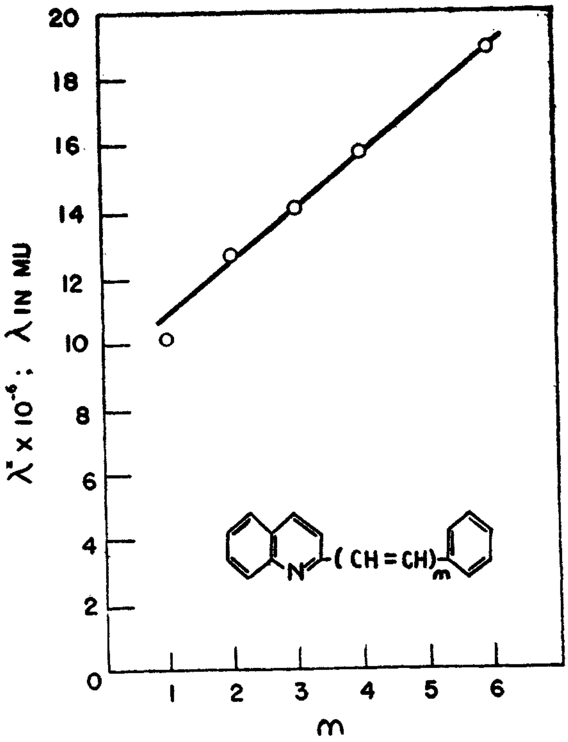

FIG. 3. Plot of the square of the wave length against the number of exocyclic double bonds.

EXPERIMENTAL

All melting points are corrected.

1-(α-Quinolyl)-2-phenylethylene(III, n = 1). This compound was prepared by the procedure of Pfeiffer *et al.* (4) with minor modifications. It melted at 98.4–98.6° (recorded m.p. 96°).

1-(α-Quinolyl)-4-phenylbutadiene-1,3 (III, n = 2). Method A. A mixture of 30 g. (0.23 mole) of freshly distilled cinnamaldehyde, 25 g. (0.18 mole) of freshly distilled quinaldine, and 3 g. of zinc chloride in a 200-cc. flask equipped with a reflux condenser was heated in an oil-bath to 115° for six hours. After cooling, 75 cc. of ethanol was added to the mixture, and the crystals which separated upon standing were washed with cold ethanol. Five recrystallizations from ethanol, including two treatments with Norit, gave 6.3 g. (13.5%) of the pure diene in form of shiny, greenish-yellow plates of m.p. 116.8–117.4° (recorded m.p. 117°).

Method B. A mixture of 6.6 g. (0.045 mole) of freshly distilled cinnamaldehyde, 7.2 g. (0.05 mole) of freshly distilled quinaldine, 2 g. of piperidine acetate and 35 cc. of 70% ethanol was kept at room temperature for forty days. The semicrystalline, dark-colored precipitate which had formed was filtered and dissolved in 35 cc. of ethanol. Upon cooling of the solution a yellowish, crystalline precipitate was slowly formed. After three recrystallizations from ethanol, including two treatments with Norit, 0.75 g. (6%) of a greenish-yellow material of m.p. 117.2–117.4° was obtained.

1-(α-Quinolyl)-6-phenylhexatriene-1,3,5 (III, n = 3). This compound was prepared from 5-phenylpentadienal (8) and quinoline by a method analogous to A, described above, except that the heating was carried out at 100°. The purest product which was obtained in a yield of 10.5% melted at 160.2–160.6° and crystallized from ethanol in form of golden-yellow plates. It is soluble in ethanol (1 part in 60 cc.), ether, benzene, and chloroform.

Anal. Calc'd for $C_{21}H_{17}N$: C, 89.01; H, 6.04.
Found: C, 88.84; H, 6.08.

1-(α-Quinolyl)-8-phenyloctatetraene-1,3,5,7 (III, n = 4). A mixture of 1.1 g. (0.006 mole) of 7-phenylheptatrienal (6) and 1.8 g. (0.012 mole) of freshly distilled quinaldine was heated gently in a test tube fitted with a stopper containing a capillary until the solid aldehyde had dissolved. About 0.2 g. of zinc chloride was added to the mixture which was then heated in an oil-bath for 70 minutes at 110°. The solid material was filtered, washed with cold ethanol and dried. It consisted of 0.6 g. of orange colored plates. The polyene was recrystallized three times from toluene, including two treatments with Norit, and finally from ethanol by continuous extraction through a thimble. The pure product, which was obtained in a yield of 10.7%, formed orange plates and melted at 194.8–195.6°. It is only slightly soluble in hot ethanol, and soluble in benzene, ether and chloroform.

Anal. Calc'd for $C_{23}H_{19}N$: C, 89.28; H, 6.19.
Found: C, 89.28; H, 6.17.

1-(α-Quinolyl)-12-phenyldodecahexaene-1,3,5,7,9,11 (III, n = 6). A mixture of 2 g. (0.0085 mole) of 11-phenylundecapentaenal (6), 15 g. (0.1 mole) of freshly distilled quinaldine, and 0.3 g. of zinc chloride was heated as described above for twenty-five hours at 97°. The dark red precipitate which had formed was filtered, washed with ethanol, and extracted from a thimble with hot toluene, an operation which took several days. Concentration of the extract gave a reddish, crystalline precipitate, which was washed with toluene, and once more recrystallized from this solvent. The final product, yield 4%, consisted of small, coppery-red plates, and melted at 232.4–232.8°. It is practically insoluble in ethanol, sparingly soluble in hot benzene and toluene, and soluble in chloroform to the extent of 3 mg. in 200 cc.

Anal. Calc'd for $C_{27}H_{23}N$: C, 89.71; H, 6.41.
Found: C, 89.24; H, 6.37.

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SUMMARY

A series of α-(α-quinolyl)-ω-phenylpolyenes has been prepared, and their absorption spectra have been measured and compared with those of the diphenylpolyene series.

It has been demonstrated that in the heterocyclic polyene series the chromophoric character of the α-quinolyl group is equivalent to that of a styryl group.

It has been shown that the relation $\lambda^2 = kn$ holds true in the α-(α-quinolyl)-ω-phenylpolyene series.

NEW HAVEN, CONN.

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