POLYNUCLEAR HETEROCYCLIC COMPOUNDS

XXII. Ultraviolet Absorption Spectra of Cyclization Products of Diindandionylmethanes*

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Spectroscopic constants of dibenzoylenepyrans, dibenzoylene-1, 4-dihydropyridine, and dibenzoylenepyridines are given. It is shown that the UV spectrum bands of dibenzoylenepyrans are slightly displaced when substituents are changed. Both in character and in band position the absorption curves for dibenzoylene-1, 4-dihydropyridines differ from those of the simpler 1, 4-dihydropyridines, and the maxima are displaced in a way depending on the substituents. On the other hand, the spectra of anyldibenzoylenepyridines are almost identical, and coincide with the spectrum of dibenzoylenepyridine.

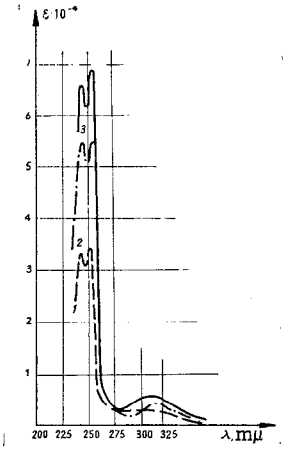
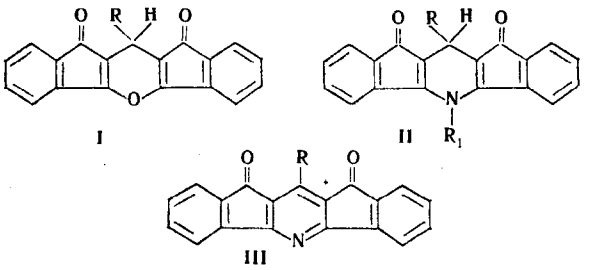


Fig. 1. UV spectra of derivatives of dibenzoylenepyrans: 1) phenyldibenzoylenepyran; 2) p-bromophenyldibenzoylenepyran; 3) isopropyldibenzoylenepyran.

In previous papers we showed [1–4] that diindandionylmethane derivatives can undergo cyclization to complex heterocyclic systems: dibenzoylenepyrans (I) and dibenzoylene-1,4-dihydropyridines (II), which latter are readily oxidized to dibenzoylenepyridines (III) [5, 6]. Some of these compounds have already been characterized by their UV spectra [4, 5, 7–9]. The UV spectra of a series of hitherto uninvestigated derivatives are determined, to investigate the general spectroscopic character of compounds of that group.

Dibenzoylenepyrans have a characteristic absorption curve whose bands are slightly displaced when the substituents in the pyran ring are changed. The characteristic intense absorption of alkyl, aryl, and furyldibenzoylenepyrans lie in a narrow range, inside the limits 243–255 mμ, and it is split into two peaks, at 243–245 and 250–255 mμ (Fig. 1) [4, 7, 8]. The intensity of the absorption spectra is greatly enhanced compared with those of diindandionyl derivatives [4, 7, 8], due to conjugation in all systems, the oxygen atom on account of its two unpaired electrons interacting with both chromophoric groups of the molecule. A low intensity band at 300–320 mμ is also characteristic, possibly due to absorption by a ketone group in the chromophoric α,β unsaturated ketone system [10]. The absorption curves of these dibenzoylenepyrans are almost identical with one another, and differ only with respect to intensities. If the pyran ring substituent is more complex, e.g., in phenanthrene, acenaphthene, the spectrum is characterized by an intense band with no splitting of the maximum. In the case of bisdimethoxybenzoylenepyran, the long wave band is shifted bathochromically (Table 1). The spectra of the dibenzoylenepyrans were observed in chloroform only (0.001 M), because of their low solubilities in other solvents.



The literature already contains data for the UV absorption spectra of 1,4-dihydropyridines, whose absorption bands are displaced in a way depending on the substituents. If the curves for dibenzoylene-1,4-dihydropyridines are compared with those of the simpler 1,4 dihydropyridines, a considerable difference is seen. The structurally simple 1,4-dihydropyridines

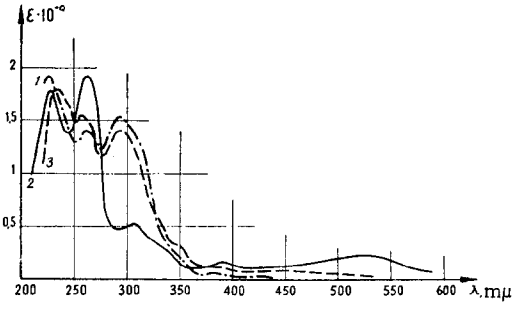


Fig. 2. UV spectra of dibenzoylenedihydropyridines (II) (0.0001 M): 1) Dibenzoylenedihydropyridine; 2) in ethanol; 3) in alkaline ethanol solution.

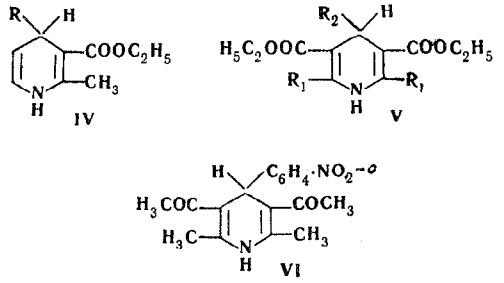
*For Part XXI see [6].

Table 1

UV Absorption Spectra of Derivatives of Derivatives of Dibenzoylenepyrans (I)

Compound	λ_{max}, mμ (ε · 10⁻⁴)
Phenyldibenzoylenepyran [3]	243(3.31), 251(3.42), 310(0.30)
p-Chlorophenyldibenzoylenepyran [6]	244(6.40), 251(6.50), 307(0.45)
p-Bromophenyldibenzoylenepyran [6]	244(6.60), 251(6.84), 314(0.55)
p-Iodophenyldibenzoylenepyran [7]	245(7.02), 252(7.22), 316(0.45)
5-Bromofuryldibenzoylenepyran [8]	244(5.94), 250(6.20), 318(0.44)
5-Iodofuryldibenzoylenepyran [8]	245(6.84), 251(7.00), 318(0.58)
Isopropyldibenzoylenepyran [4]	245(5.45), 255(5.50), 315(0.40)
Acenaphthenonespirodibenzoylenepyran [2]	252(5.76), 318(0.96)
4-Nitrophenanthrenonespirodibenzoylenepyran [20]	248(8.80), 320(0.95)
Acenaphthenonespirobis(dimethoxybenzoylene)pyran [21]	252(5.62), 345(1.44)
Phenanthrenonespirobis(dimethoxybenzoylene)pyran	255(8.20), 348(1.24)

(IV, V, VI) are characterized by two intense bands in the ultraviolet region of the spectrum, lying in the intervals 210–260 and 330–380 mμ and influenced by the substituents: if IVb absorbs at 210 and 330 mμ, the long wave band of IVa is shifted to 350 mμ [11], Va has two intense absorption maxima at 220 and 375 mμ [12] while the maxima of Vb and Vc lie at about 240 and 350 mμ [13, 14]. In isolated cases compounds of similar structure show yet a third maximum at about 260–280 mμ (Vd) [13, 15]. When the ethoxycarbonyl group at positions 3 and 5 is replaced by acetyl, the long wave band is, for example, shifted to 380 mμ. Ve absorbs at 237 and 332 mμ, while the maxima for VI are at 257 and 382 mμ [15].



IV V VI

a R = H
b R = CH_3

a $R_1 = R_2 = H$
b $R_1 = R_2 = CH_3$
c $R_1 = CH_3$; $R_2 = C_6H_5$
d $R_1 = CH_3$; $R_2 = p\text{-}NO_2 \cdot C_6H_4$
e $R_1 = CH_3$; $R_2 = o\text{-}NO_2 \cdot C_6H_4$

In decahydroacridinedione systems, where the dihydropyridine ring is condensed with two alicyclic 6-membered rings, the ordinary absorption bands of 1, 4-dihydropyridines are conserved, since conjugation of the system is not enhanced [16]. Benzoylene- [16, 17] and dibenzoylene-1,4-dihydropyridines (II) [5, 9] where the dihydropyridine ring is condensed with one or two 5-membered rings, exhibit spectra of quite a different kind, and this is connected with increased conjugation in the entire system. These compounds have intense absorption bands at 220–240 mμ and 250–260 mμ, while in the longer wave region (above 300 mμ), there are only absorption bands of low intensity; the band at about 300 mμ is probably the R-band of carbonyl groups [10, 17, 18], whereas in the visible part of the spectrum there is a wide absorption band in the 480–560 mμ interval, causing the red color of the compound.

As unsubstituted dibenzoylenedihydropyridine [6] (II, R = R° = H) is only slightly soluble in organic solvents, the UV spectrum observed is that of its anion in alkaline solution (Fig. 2) only. Phenyldibenzoylenedihydropyridine (II, R = C_6H_5, R° = H) in ethanol solutions has two intense absorption maxima at 228 and 262 mμ, and low-intensity absorption distributed at 307 and 525 mμ (Fig. 2). Similar spectra are exhibited by its halogen derivatives (Fig. 3), and by nitrophenyl- and alkyldibenzoylenedihydropyridines (Table 2). When the hydrogen at the nitrogen is substituted by the phenyl group, the characteristic maxima are preserved. In chloroform solution only a 260 mμ band with enhanced intensity [5] appears (Fig. 3).

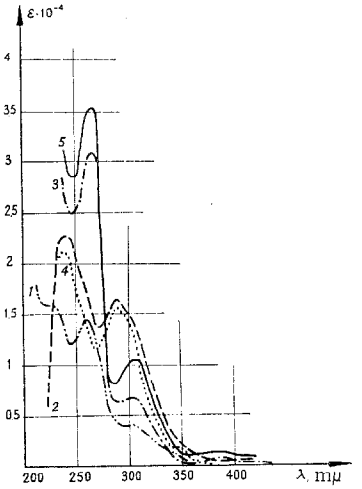


Fig. 3. UV spectra of halogenophenyldibenzoylenedihydropyridines: (II) (0.0001 M) 2,4-dichlorophenyldibenzoylenedihydropyridine: 1) in ethanol; 2) in alkaline ethanol solution; 3) in chloroform; p-bromophenyldibenzoylenedihydropyridine: 4) in alkaline ethanol solution; 5) in chloroform.

Dibenzoylenedihydropyridines are known to form a strongly greenish-blue anion in alkaline solution [1, 19]. The absorption curves of the anions in the near ultraviolet resemble the plots for the corresponding dibenzoylenedihydropyridines in ethanol solution save

Table 2

UV Absorption Spectra of Derivatives of Dibenzoylene-1,4-dihydropyridines (II)*

	Solvent	λ_{max}, mμ (ε · 10⁻⁴)
Dibenzoylenedihydropyridine [6]	C_2H_5OH+NaOH	225(2.49), 261(1.42), 294(1.54), 380(0.08), 700(0.44)
Phenyldibenzoylenedihydropyridine [5]	C_2H_5OH	228(1.79), 262(1.93), 307(0.52), 388(0.14), 525(0.23)
The same	$CHCl_3$	233(3.03), 262(3.40), 305(0.85), 386(0.18), 510(0.28)
"	C_2H_5OH+NaOH	235(1.79), 255(1.55), 292(1.41), 440(0.09), 650(0.56)
N-Phenyl-4-phenyldibenzoylenedihydropyridine	C_2H_5OH	231(3.01), 262(2.40), 308(0.65), 390(0.14)
The same	$CHCl_3$	237(2.10), 264(2.49), 308(0.65), 390(0.16)
m-Nitrophenyldibenzoylenedihydropyridine	C_2H_5OH+NaOH	233(2.04), 252(2.05), 285(1.80), 347(0.44), 650(0.56)
N-Phenyl-4-(m-nitrophenyl)dibenzoylenedihydropyridine [3]	C_2H_5OH**	230(2.44), 262(2.12), 405(1.80), 520(0.16)
The same	$CHCl_3$	— 264(3.22), 308(0.87), 390(0.25), 525(0.30)
p-Chlorophenyldibenzoylenedihydropyridine [6]	C_2H_5OH	226(1.41), 260(1.35), 302(0.40),
The same	$CHCl_3$	— 265(3.66), 303(0.80),
"	C_2H_5OH+NaOH	235(2.59), 288(1.79), 347(0.37), 430(0.07)
p-Bromophenyldibenzoylenedihydropyridine [6]	$CHCl_3$	— 267(3.54), 307(1.05), 385(0.13)
The same	C_2H_5OH+NaOH	237(2.13), 288(1.55), 348(0.22),
p-Iodophenyldibenzoylenedihydropyridine [6]	$CHCl_3$	— 261(3.09), 306(1.08),
The same	C_2H_5OH+NaOH	236(2.83), 287(1.67), 350(0.55)
2,4-Dichlorophenyldibenzoylenedihydropyridine [6]	C_2H_5OH	228(1.67), 260(1.48), 305(0.40), 410(0.09)
The same	$CHCl_3$	— 263(3.09), 304(0.69), 386(0.08)
"	C_2H_5OH+NaOH	244(2.26), 289(1.65), 440(0.13), 650(0.47)
Isopropyldibenzoylenedihydropyridine	C_2H_5OH	226(3.05), 262(3.10), 305(0.62), 530(0.20)
The same	C_2H_5OH+NaOH	236(2.30), 280(1.78), 660(0.66)
Phenanthrenonespirodibenzoylenedihydropyridine [1]	C_2H_5OH+NaOH	245(4.52), 259(4.40) M, 275(2.84) M, 635(0.80)
4-Nitrophenanthrenonespirodibenzoylenedihydropyridine [20]	C_2H_5OH+NaOH	239(5.20), 310(1.90) M, 635(0.80)
Acenaphthenonespirodibenzoylenedihydropyridine [9]	$CHCl_3$	241(3.48), 255(3.30) M, 322(1.06), 405(0.34), 557(0.30)
The same	CH_3OH+NaOH	244(3.27), 250(3.26) M, 288(2.02), 440(0.22), 640(0.66)

*Solution concentration 0.0001 M.

**Solution concentration 0.00005 M.

that the bands are displaced bathochromically, the maxima being at 233–244 and 287–289 mμ. This may indicate that in ethanol solution the structure of the dibenzoylenedihydropyridines resembles that of the anion, i.e., the electron density is more or less uniform in both cases.

The spectra of the anion of dibenzoylenedihydropyridine itself and of its 4-phenyl derivative exhibit yet a third absorption band at 255 and 261 mμ respectively (Fig. 2). In the visible part of the spectrum there is a wide absorption band in the interval 600–700 mμ (not shown in the figure), characteristic of the anion of dibenzoylenedihydropyridine.

If the position 4 substituent in the dibenzoylenedihydropyridines is more complex, e.g., phenanthrene, acenaphthene [9], the near UV spectra are shifted hypsochromically (Table 2). Because dibenzoylenedihydropyridines with complex substituents have very low solubilities in the usual organic solvents, comparison of their spectra is difficult.

A completely different spectrum picture is shown by the oxidation products of dibenzoylenedihydropyridines, i.e., dibenzoylenepyridines (III) because their chromophoric system has changed. The spectrum of dibenzoylenepyridine itself is characterized by two intense absorption bands at 267–269 and 310 mμ, while at 381 mμ there is a low-intensity maximum (Fig. 4). The same character is retained in the spectra of phenyl [5] and halogenophenyldibenzoylenepyridines (Table 3).

The UV spectra were determined with an SF-4 instrument.

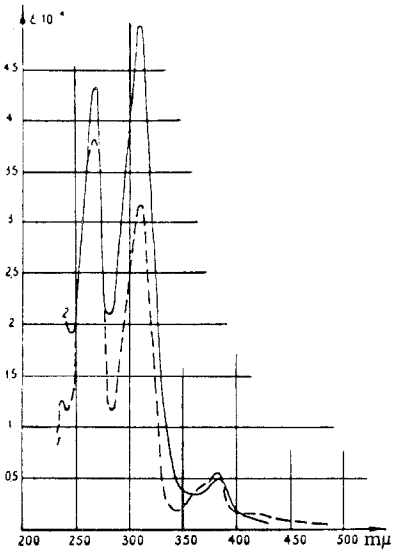


Fig. 4. UV spectra of dibenzoylenepyridines (III) in chloroform (0.0001 M): 1) dibenzoylenepyridine; 2) p-bromodibenzoylenepyridine.

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Table 3

UV Absorption Spectra of Derivatives of Dibenzoylenepyridines (III)*

Compound	λ_{max}, mμ (ε · 10⁻⁴)
Dibenzoylenepyridine [22]	237(1.24), 267(3.84), 310(3.17), 381(0.55)
Phenyldibenzoylenepyridine [5]	267(4.45), 307(4.80), 380(0.55)
p-Chlorophenyldibenzoylenepyridine [6]	268(4.00), 309(4.65), 383(0.54)
p-Bromophenyldibenzoylenepyridine [6]	268(4.33), 310(4.96), 383(0.50)
p-Iodophenyldibenzoylenepyridine [6]	270(4.00), 310(4.90), 385(0.52)
2, 4-Dichlorophenyldibenzoylenepyridine [6]	269(4.31), 310(4.05), 382(0.60)

*Spectra measured with a 0.0001 M $CHCl_3$ solution.

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