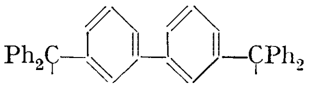
70. *The Absorption Spectra of the Phenylpyridines and Pyridyldiphenyls.*

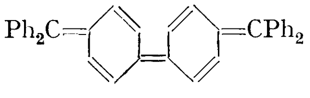
By A. E. Gillam, D. H. Hey, and A. Lambert.

A comparison of the absorption spectra of the phenylpyridines and the 3- and 4-pyridyldiphenyls with those of diphenyl, *m*-terphenyl, and *p*-terphenyl respectively reveals a close resemblance, which indicates that the internuclear bond between two benzene nuclei and that between a benzene and a pyridine nucleus are similar in character.

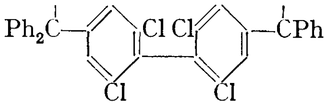
Information concerning the nature of the carbon–carbon bond uniting two aromatic rings, *e.g.*, the internuclear bond in diphenyl and its derivatives, has been obtained from a wide variety of sources which include chemical evidence, measurements of dipole moments, absorption spectra, and optical activity, as well as the computation of bond lengths by *X*-ray analysis and mathematical calculation. The conclusions reached indicate that the internuclear bond in compounds of the diphenyl type is hybrid in nature and possesses some measure of double-bond character, and this form of conjugation between aromatic nuclei may be responsible for the maintenance of such structures in a planar form (cf. Le Fèvre and Le Fèvre, J., 1936, 1130; Gillam and Hey, J., 1939, 1170). Moreover, the character of the bond is profoundly influenced by the presence of substituent groups at the ortho-positions. Further evidence on the latter aspect of the problem may be found in measurements of the magnetic susceptibility of diradicals in the diphenyl and terphenyl series. It has been shown that whereas *mm'*-diphenylenebisdiphenylmethyl (I) exists mainly as a true diradical, the isomeric *pp'*-compound appears to exist in the molecular quinonoid form (II) (Müller and Müller-Rodloff, *Annalen*, 1935, **517**, 134); if, however, the ortho-positions with respect to the internuclear bond in the second isomeride are suitably substituted, as in 2 : 6 : 2' : 6'-tetrachlorodiphenylene-*pp'*-bisdiphenylmethyl (III), the diradical form is stabilised by the non-planar configuration imposed on the molecule, and



(I.)



(II.)



(III.)

passage into the molecular quinonoid form is suppressed (Müller and Neuhoff, *Ber.*, 1939, **72**, 2063). Further examples of this phenomenon have been recorded by Müller and Tietz (*Naturwiss.*, 1940, **28**, 189) and by Theilacker and Ozegowski (*Ber.*, 1940, **73**, 33).

In contrast, information concerning the nature of the carbon–carbon bond uniting a benzenoid nucleus to that of pyridine is almost non-existent apart from a few abortive attempts to detect optical activity in suitably substituted arylpyridines (Chalmers, Lions, and Robson, *J. Proc. Roy. Soc. N.S.W.*, 1930, **64**, 320; Steele and Adams, *J. Amer. Chem. Soc.*, 1930, **52**, 4528; Lions, *ibid.*, 1931, **53**, 1176; Adams and Yuan, *Chem. Reviews*, 1933, **12**, 261). On the other hand, Woodruff and Adams (*J. Amer. Chem. Soc.*, 1932, **54**, 1977) were able to resolve a substituted dipyridyl, *viz.*, 2 : 4 : 2′ : 4′-tetracarboxy-6 : 6′-diphenyl-3 : 3′-dipyridyl, which readily underwent racemisation. More recently, Breckenridge and Smith (*Canadian J. Res.*, 1938, **16**, B, 109) have reported a failure to resolve 2-*o*-carboxyphenylpyridine-3-carboxylic acid but obtained a partial resolution of the methiodide of its dimethyl ester by the method of asymmetric induction.

In a previous communication (Gillam and Hey, *loc. cit.*) a study was made of the absorption spectra of a number of hydrocarbons consisting of chains of benzene nuclei united at either the *m*- or the *p*-positions, and for purposes of comparison a similar study has now been made of the phenylpyridines and pyridyldiphenyls.

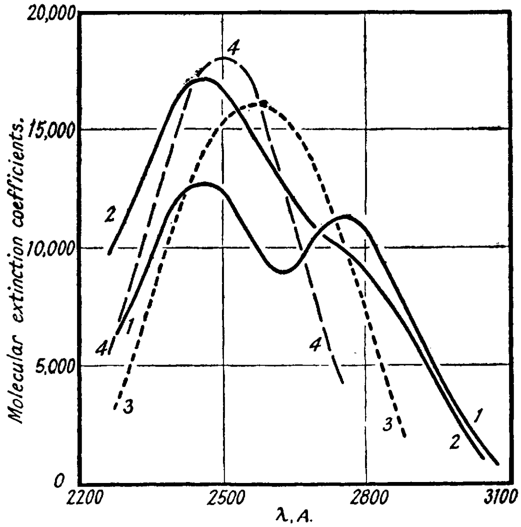
Benzene itself exhibits a highly characteristic absorption spectrum, the curve of which contains a group of eight maxima ranging from 2280 to 2700 A. and another more intense band near 2000 A. From the low intensity of the absorption in the neighbourhood of 2550 A. (ε = approx. 200), it is probable that this group of absorption bands is not that characteristic of the conjugated system, whereas the band near 2000 A. has the intensity of absorption usually associated with such a system (ε for benzene at 2000 A. = 7940). When an ethylenic double bond is attached to the benzene nucleus, as in styrene, the increase in conjugation causes a movement of the short-wave absorption band towards longer wavelengths, *i.e.*, to λ max. = 2445, ε = *ca.* 14,000 (Pestemer and Wiligut, *Monatsh.*, 1935, **66**, 119). When two benzene nuclei are joined together, as in diphenyl, the conjugated system so produced gives rise to an absorption spectrum differing from that of benzene in being more intense (ε = 18,000—20,000) and in exhibiting the new band as a smooth curve without the fine structure characteristic of benzene. Here again it is probable that the maximum near 2000 A. in the absorption curve of benzene has been displaced by the conjugation to 2500 A. in diphenyl, and that this intense absorption completely masks the more characteristic but less intense group of bands with its centre near 2550 A. which is also exhibited by benzene (cf. Gillam and Hey, *loc. cit.*). Pyridine exhibits an absorption spectrum similar to but somewhat more intense than that of benzene. When, however, a benzene nucleus is joined to a pyridine nucleus, as in the phenylpyridines, the light absorption clearly indicates that a system is formed similar to that in diphenyl. The three isomeric phenylpyridines exhibit absorption spectra which, although similar in type, are sufficiently distinct to be used as a means of differentiation. The data are shown in Fig. 1 and in the following table.

	λ max., A.	ε.	Solvent.		λ max., A.	ε.	Solvent.
Benzene	1970 2550	7940 244	Alcohol[1]	β-Phenylpyridine	2460 (2750)	17,200 10,000	Alcohol
Pyridine	2530	1820	Alcohol[1]	γ-Phenylpyridine	2570	16,000	Alcohol
Styrene	2445	14,000	Hexane[2]	$\alpha\alpha'$-Dipyridyl	2370 2810	10,890 14,500	Hexane
Diphenyl	2500	18,000	Alcohol[3]				
α-Phenylpyridine	2455 2755	12,700 11,300	Alcohol	$\gamma\gamma'$-Dipyridyl	2385	12,600	Hexane

[1] Values from curves in "International Critical Tables," **5**, 363. [2] Pestemer and Wiligut, *loc. cit.* [3] Gillam and Hey, *loc. cit.*

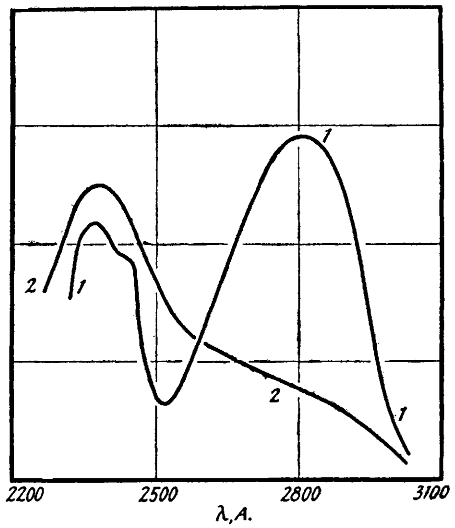
The absorption spectra of the α- and β-phenylpyridines have in common the fact that the curves exhibit two maxima (or incipient maxima) at approximately the same wave-lengths (cf. Fig. 1). They differ, however, in that whereas for the α-isomeride the two maxima are well defined and of about the same intensity, yet the curve for the β-isomeride exhibits only one good maximum, the other being only an inflexion on the curve at a much lower intensity of absorption. This might suggest that the two substances examined are not separate entities but mixtures of two components in variable proportions. However, the method of preparation, involving the liberation of the free bases from the pure crystallised picrates, gives no support to this contention. The absorption spectra of $\alpha\alpha'$- and $\gamma\gamma'$-dipyridyl have also been examined (Table and Fig. 2) for comparison. The former reveals two well-defined maxima similar to those shown by α-phenylpyridine.

FIG. 1.



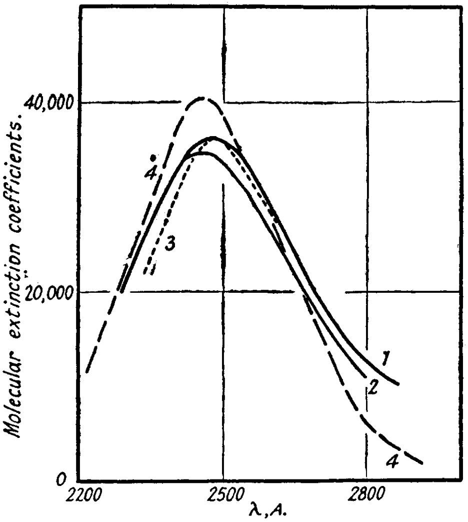
Absorption spectra (in alcohol).
1. *α-Phenylpyridine.*
2. *β-Phenylpyridine.*
3. *γ-Phenylpyridine.*
4. *Diphenyl.*

FIG. 2.



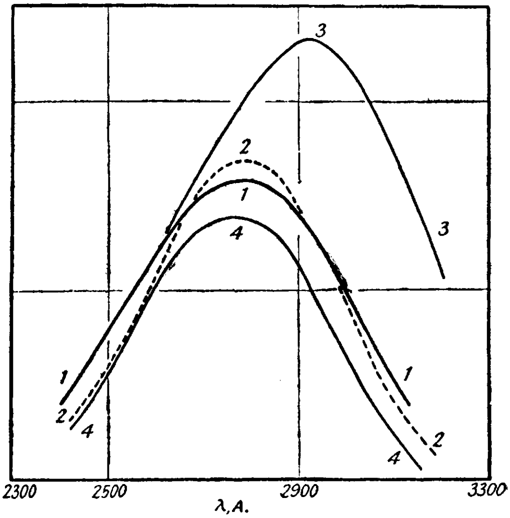
Absorption spectra (in hexane).
1. *αα′-Dipyridyl.*
2. *γγ′-Dipyridyl.*

FIG. 3.



Absorption spectra (in hexane).
1. 3-*γ-Pyridyldiphenyl* (VI).
2. 3-*β-Pyridyldiphenyl* (V).
3. 3-*α-Pyridyldiphenyl* (IV).
4. m-*Terphenyl.*

FIG. 4.

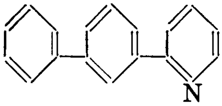


Absorption spectra (in hexane).
1. 4-*β-Pyridyldiphenyl* (VIII).
2. 4-*γ-Pyridyldiphenyl* (IX).
3. 4-*α-Pyridyldiphenyl* (VII).
4. p-*Terphenyl.*

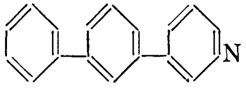
The absorption spectra of the three isomeric **3**-pyridyldiphenyls are so closely similar as to be almost identical with each other and with the absorption of *m*-terphenyl (see table and Fig. **3**). It is thus probable that, as in the case of the latter hydrocarbon, conjugation does not extend beyond two nuclei (cf. Gillam and Hey, *loc. cit.*). On the other hand, with the three isomeric 4-pyridyldiphenyls (see table and Fig. 4), as with *p*-terphenyl where conjugation can exist through the whole molecule, it is found that the absorption band is displaced to longer wave-lengths. Further, whereas the absorption spectra of the 4-β- and 4-γ-pyridyldiphenyls are similar to each other and to that of *p*-terphenyl in both location and intensity, yet 4-α-pyridyldiphenyl exhibits a somewhat more intense band displaced yet further to longer wave-lengths.

Absorption spectra of 3-*pyridyldiphenyls in hexane.*

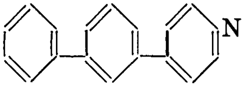
	λ max., A.	ε.		λ max., A.	ε.
3-α-Pyridyldiphenyl (IV) ...	2480	36,000	3-γ-Pyridyldiphenyl (VI) ...	2480	36,000
3-β-Pyridyldiphenyl (V)	2455	35,000	*m*-Terphenyl	2465	40,500



(IV.)



(V.)

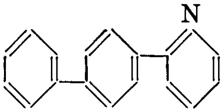


(VI.)

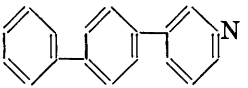
Absorption spectra of 4-*pyridyldiphenyls in hexane.*

	λ max., A.	ε.		λ max., A.	ε.
4-α-Pyridyldiphenyl (VII) ...	2920	45,500	4-γ-Pyridyldiphenyl (IX) ...	2790	33,500
4-β-Pyridyldiphenyl (VIII)...	2790	31,000	*p*-Terphenyl	2760	27,860 *

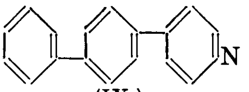
* This is an amended value. The curve and value for ε for *p*-terphenyl in hexane solution were previously incorrectly recorded (Gillam and Hey, *loc. cit.*).



(VII.)



(VIII.)



(IX.)

The absorption spectra of the phenylpyridines and the **3**- and the **4**-pyridyldiphenyls thus show a strong resemblance to those exhibited by diphenyl, *m*-terphenyl, and *p*-terphenyl respectively, indicating that the internuclear bond uniting a pyridine nucleus to a benzene nucleus is similar in character to that uniting two benzene nuclei with reference to the propagation of conjugation between the nuclei.

EXPERIMENTAL.

Determination of Absorption Spectra.—Measurements were carried out on a Hilger E_3 quartz spectrograph used in conjunction with a Spekker photometer. The notation used for the absorption data is that generally accepted, but for details see Gillam and Hey (*loc. cit.*).

Compounds.—The α-, β-, and γ-phenylpyridines were prepared by the method of Haworth, Heilbron, and Hey (J., **1940**, 349), the free bases being regenerated from the pure picrates by warming with alkali. A specimen of α-phenylpyridine was also prepared by the method of Evans and Allen (*Organic Syntheses*, **1938**, **18**, 70). The six pyridyldiphenyls were prepared by the method of Heilbron, Hey, and Lambert (J., **1940**, 1279). The specimens of αα′- and γγ′-dipyridyl were purchased from The British Drug Houses, Ltd., the latter as hydrochloride.

This work formed part of a larger programme which, owing to the present emergency, has had to be curtailed. The data now placed on record refer only to that portion of the work which is sufficiently complete for publication.

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