higher are negligible compared to unity and may be dropped from the series in brackets to give

$$q_n^*(s) = \left[q_n(s) - \frac{4D\sigma_3}{\omega^2x^2}\frac{dq_n(s)}{ds}\right] + \frac{D}{\omega^4}\left(\frac{\sigma_1}{x^2t}\right)\left[\frac{d^2q_n(s)}{ds^2} - \frac{4D\sigma_5}{\omega^2x^2}\frac{d^3q_n(s)}{ds^3}\right] + \frac{1}{2}\frac{D^2}{\omega^8}\left(\frac{\sigma_1}{x^2t}\right)^2\frac{d^4q_n(s)}{ds^4} + \ldots \quad (38)$$

The terms $\frac{4D\sigma_3}{\omega^2x^2}\frac{dq_n(s)}{ds}$ and $\frac{4D\sigma_5}{\omega^2x^2}\frac{d^3q_n(s)}{ds^3}$ are seldom more than a few per cent. of the maximum values of $q_n(s)$ and $d^2q_n(s)/ds^2$, respectively, so they may also be neglected in most experiments.

It is not evident from equation (35)that plots of $q_n^*(s)$ *versus* $\sigma_1/(x^2t)$ will extrapolate linearly to $q_n(s)$ at very long times, *i.e.*, when $s\omega^2t >> 1$. However, these plots should be quite straight over an intermediate range of times in which t is so large that terms containing the fourth and higher derivatives of $q_n(s)$ are negligible but in which $s\omega^2t$ is still small. The values of $q_n(s)$ may therefore be obtained by extrapolating these straight regions, which sometimes include most of the experimental points, to $\sigma_1/(x^2t) = 0$.

When D is not the same for all solute molecules, we start with the sedimentation spreading equation analogous to equation (12) and arrive at an expression identical to equation (35) except that $Q_n^*(s)$ is substituted for $q_n^*(s)$ and the products $D^j\frac{d^kq_n(s)}{ds^k}$, where $j = 0, 1, 2, \ldots$, and $k = 0, 1, 2, \ldots$, are replaced by $\frac{\partial^k[\overline{D_s^j}Q_n(s)]}{\partial s^k}$ in which

$$\overline{D_s^j} = \frac{\int_0^\infty D^jq_n(s,D)dD}{\int_0^\infty q_n(s,D)dD} \quad (39)$$

Since solutes which have a distribution of sedimentation constants are almost certain to have a distribution of diffusion constants, no attempt has been made to invert equation (35) or equation (38) to express $q_n(s)$ in terms of $\partial n/\partial x$ and its derivatives as was done for electrophoretic spreading in equation (20). To compute $Q_n(s)$ in this way would require a knowledge of average diffusion constants, equation (39), as a function of the sedimentation constant.

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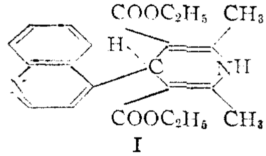
[CONTRIBUTION FROM THE WELLCOME RESEARCH LABORATORIES]

Absorption Spectra and Structure of Some 4-Arylpyridines Derived from the Hantzsch Pyridine Synthesis

BY ARTHUR P. PHILLIPS AND PHOEBE LEE GRAHAM

Comparison of the ultraviolet absorption spectra of certain 4-aryl-2,6-lutidines, both with and without 3,5-dicarbethoxy groups on the pyridine ring, reveals valuable information concerning the configuration of these compounds. When the 4-aryl is phenyl the presence of the carbethoxy groups appears to block internuclear resonance, or conjugation, relatable to coplanarity between the two rings. Conjugation, and thus presumably coplanarity, is readily apparent in 4-phenyl-2,6-lutidine in which the carbethoxys are absent. When the 4-aryl is quinoline, results suggest no significant resonance interaction between the quinoline and pyridine rings in the presence of the two carbethoxys. Absorption spectra of the quinoline derivatives also indicate little or no conjugation between rings even in the absence of carbethoxy groups.

In an earlier study[1] it was hypothesized that in certain products derived from the Hantzsch pyridine synthesis, exemplified by I, the aryl and dihydropyridine rings should be non-coaxial and non-copolar. The former suggestion derives from the concept of the tetrahedral structure of carbon, the latter is related to the currently accepted views of the structure of substituted biphenyls. This paper presents some work in support of the latter idea.



I

It has long been known[2-6] that biphenyls suitably substituted in the ortho positions are resolvable into optical antipodes. These results led to the concept of a coaxial arrangement of the two phenyls which were also capable of copolanarity in non-hindered biphenyl systems. Optical activity in this series was ascribed to molecular asymmetry depending upon restriction of rotation about the central bond, by bulky ortho groups which made copolanarity difficult or impossible through steric hindrance.

Although numerous substituted biphenyls were resolved by Adams[6] and co-workers and the earlier

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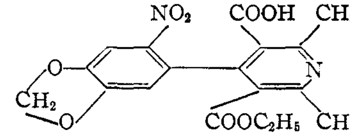
workers,[2-5] attempts[7] made to resolve certain appropriately substituted arylpyridines failed. Lions[8] reported that he was trying to resolve a phenylpyridine, II, closely related to the compounds under consideration in this paper. Since no further


II

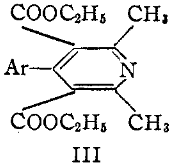
results on this have been found it is assumed that resolution was not attained. Woodruff and Adams[9] successfully resolved a substituted dipyridyl but it was very readily racemized. Because of the numerous difficulties involved in resolution procedures in general and particularly because of the lack of success with phenylpyridines it seemed desirable to try another way of showing lack of coplanarity in the compounds under investigation.

Gillam and Hey[10] in their excellent study with biphenyl and the *m*- and *p*-polyphenyls have demonstrated by means of ultraviolet absorption spectra the existence of extensive conjugation between adjacent phenyl rings. From modern resonance theory this leads to the expectation that the separate rings in biphenyl should be substantially coplanar. This prediction has been supported by X-ray studies which have also indicated appreciable double bond character for the linkage connecting the rings. In a later paper these workers[11] have presented the ultraviolet absorption spectra of the various phenylpyridines, dipyridyls and pyridylbiphenyls and have observed the same sort of relationship as for the polyphenyls, indicating conjugation or resonance interaction between the phenyl and pyridine rings.

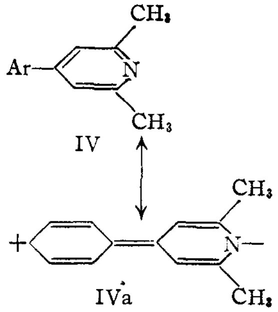
Other workers[12-16] have examined the ultraviolet absorption spectra of substituted biphenyls and found that types related to the resolvable biphenyls do not exhibit typical biphenyl spectra but show, rather, spectra resembling those of the similarly substituted benzenes.

The resolvable type of biphenyls represents an extreme case. Even those compounds found by Adams[6] to possess only brief half-life periods of optical activity must have rather large energy barriers resisting coplanarity. Many considerably less hindered systems should exist in which hindrance to the planar state is too small to permit resolution but is still sufficient to make the coplanar condition improbable and consequently to inhibit internuclear resonance. Other cases exist in which the unsymmetrical ring substitutions necessary for resolution are not present. For the identification of coplanarity, associated with resonance conjugation between the two aryl rings, or its absence, ultraviolet absorption spectrometry should provide a more delicate tool than resolution.

To enable the use of ultraviolet spectra in the solution of the current problem the aryldihydropyridines, illustrated by I, were converted by mild oxidation to the arylpyridines in which the presence of two connected aromatic nuclei should allow resonance conjugation (IV↔IVa) when coplanarity is possible.


III

Ar, phenyl or
4-quinolyl


IV

IVa

In Fig. 1 are shown the spectra of 3,5-dicarbethoxy-2,6-lutidine, 3,5-dicarbethoxy-4-phenyl-2,6-lutidine (III, Ar-phenyl), and 4-phenyl-2,6-lutidine (IV, Ar-phenyl). Comparison of the spectra of both III and IV (Ar = phenyl) with that of 4-phenylpyridine[11] indicates extensive resonance conjugation and the absence of serious steric hindrance in IV, for its spectrum is comparable in every respect ($\lambda_{max.}$ 2540 Å.; ϵ 14,100) with that of 4-phenylpyridine[11] ($\lambda_{max.}$ 2570 Å.; ϵ 16,000). In III, lacking any characteristic peak in the region of 2500 Å., restricted rotation with absence of coplanarity or conjugation is strongly indicated.

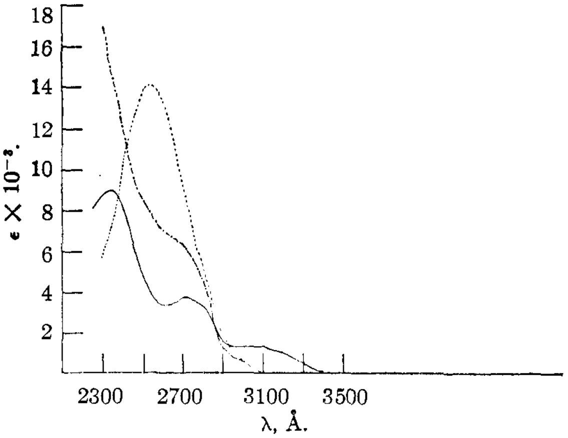


Fig. 1.—Curve 1 ——, 3,5-dicarbethoxy-2,6-lutidine; curve 2, --------, 4-phenyl-2,6-lutidine; curve 3, ·—·—·—·., 3,5-dicarbethoxy-4-phenyl-2,6-lutidine.

The corresponding spectra for the 4-(4′-quinolyl) derivatives, III and IV (Ar = 4-quinolyl), are shown in Fig. 2 along with the spectrum of quinoline itself. With these quinoline derivatives the principal peaks fall at about the same wave lengths (quinoline: $\lambda_{max.}$ 2780 Å.; ϵ 7000; III; Ar = 4-quinolyl: $\lambda_{max.}$ 2800 Å.; ϵ 17,300; IV: Ar = 4-quinolyl: $\lambda_{max.}$ 2830 Å.; ϵ 8100) and differ only moderately in intensity. Comparison of the spec-

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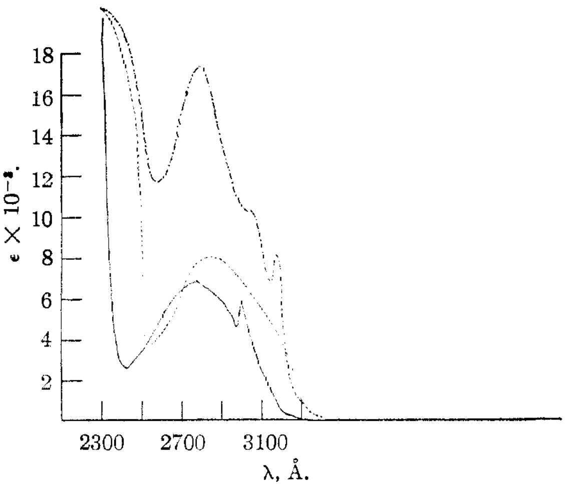

Fig. 2.—Curve 1 ——, quinoline; curve 2 --------, 4-(4'-quinolyl)-2,6-lutidine; curve 3 -·-·-·-·-, 3,5-dicarbethoxy-4-(4'-quinolyl)-2,6-lutidine.

tra of III and IV (Ar = 4-quinolyl) with those of quinoline (all in Fig. 2) and 3,5-dicarbethoxy-2,6-lutidine (Fig. 1) reveals a lack of any pronounced bathochromic shift between III and IV or between quinoline and either III or IV. The close similarity between the curves for quinoline and IV (Ar = 4-quinolyl) suggests that little if any resonance interaction between aryl rings exists in IV, although the loss of some of the quinoline fine structure in IV indicates some resonance between rings may persist. By analogy with the phenyl derivatives (III and IV, Ar = phenyl) it seems inconceivable that coplanarity of rings should be more likely in the quinoline derivatives (III and IV). In III (Ar = 4-quinolyl) the benzenoid ring of the quinoline should offer considerable hindrance to coplanarity by interfering with the carbethoxys on the pyridine ring, while in IV less resistance, between the hydrogens on the pyridine and the benzenoid ring of quinoline, should be expected. Thus for III (Ar = 4-quinolyl) coplanarity and resonance interaction should be completely excluded, while the lack of any significant bathochromic shift between quinoline, III, or IV suggests little conjugation in either of the latter two.

At present no satisfactory explanation can be offered to account for the intense absorption of III (Ar = 4-quinolyl) at 2800 Å., the curve for which is only partially accounted for by the summation of the curves of quinoline and of 3,5-dicarbethoxy-2,6-lutidine.

The conclusions relating to structure derived from the curves shown in Figs. 1 and 2 are not strictly transferable to the dihydro precursors of III in which the two rings are not coaxial and therefore are not coplanar for that reason alone. Because of the large steric stresses at the 4-position of the dihydropyridines under consideration the normal tetrahedral bond arrangement about that carbon may be considerably modified to allow a closer approximation to coaxiality between rings here than when such stresses do not exist. If this were true then lack of coplanarity would be related principally to rotation of one ring about the "almost coaxial" axis of the two rings.

Experimental

Determination of Absorption Spectra.—Measurements were carried out on a Beckman quartz spectrophotometer, Model D.U., cell length 1 cm. The solutions were run at a concentration of 10 mg./liter in 95% ethanol.

Compounds.—The dihydropyridine intermediates for 3,5-dicarbethoxy-2,6-lutidine and its 4-phenyl- and 4-(4'-quinolyl)-derivatives were made by modifications[1] of the original Hantzsch[17] procedure. The completely aromatic products were obtained by oxidation of the dihydro compounds with 4 *N* nitric acid. After precipitating the bases with aqueous ammonia the products (3,5-dicarbethoxy-2,6-lutidine,[18] 3,5-dicarbethoxy-4-phenyl-2,6-lutidine[19]; and 3,5-dicarbethoxy-4-(4'-quinolyl)-2,6-lutidine[1]) were purified by recrystallization from Skellysolve B.

The compounds III (Ar = phenyl or 4-quinolyl) were saponified and decarboxylated to give the compounds IV (Ar = phenyl[20] or 4-quinolyl[21]) by the procedure of Heilbron and co-workers.[21]

All the compounds synthesized for spectral study were purified by several recrystallizations and gave satisfactory analyses for carbon and hydrogen.

TUCKAHOE 7, NEW YORK RECEIVED SEPTEMBER 21, 1951

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