425. *Studies in the Pyrroline Series. Part IV.*[1] *The Ultraviolet Absorption of the Unconjugated Azomethine Group*

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A weak broad band in the ultraviolet spectra of alkyl-1-pyrrolines is observed, and it is suggested that this is due to the $n \rightarrow \pi^*$ transition of the azomethine group. Support for this suggestion comes from studies of spectra and optical rotatory dispersion of open-chain azomethines, notably neopentylidene derivatives.

THERE is much literature on the carbonyl chromophore,[2] and the light absorption of the thiocarbonyl system is well known.[2,3] It is curious that the spectral properties of the simple azomethine group should not have attracted some attention. Although the conjugated,[4] arylated,[5] and enaminised [6] systems are familiar, the unconjugated azomethine chromophore has never been properly recognised and many recent summaries suggest, explicitly [7] or by omission, that this chromophore has no important absorption in the near-ultraviolet region (>200 mμ). Examples are, indeed, very few. Hires and Balog [8] reported absorption for *N*-n-butylidene-n-butylamine [$\lambda_{max.}$ (EtOH) 233 mμ, log ε 2·19] and *N*-isobutylidene-n-butylamine [$\lambda_{max.}$ (EtOH) 233 mμ, log ε 2·16] while data for *N*-isobutylidenecyclohexylamine [$\lambda_{max.}$ (cyclohexane) 245 mμ, log ε 1·87] and *N*-isopropylidenemethylamine ($\lambda_{max.}$ 230 mμ) have been quoted in reviews.[9,10]

The availability of a series of purified 1-pyrrolines has now made possible the investigation of this chromophore in a saturated ring system. An example of such a chromophore has previously been recorded without comment (4,5-trimethylene-2-methyl-1-pyrroline; $\lambda_{max.}$ 229 mμ, log ε 2·29),[11] and an inflection at *ca.* 235 mμ in the spectrum of 3-spirocyclopropyl-2-methyl-1-pyrroline has been observed but attributed to a conjugation effect.[12] An intriguing example of the three-membered ring system, 2-butylazir-1-ine, is reported [13] to have $\lambda_{max.}$ (cyclohexane) 229 mμ, log ε 2·05, but in certain more complex examples of cyclic azomethines a maximum has not been observed.[14] The present study indicates that 1-pyrrolines bearing only alkyl substituents possess a weak broad band in the 225 mμ region (Table 1).

Since the region of the spectrum in question is particularly susceptible to the effect of impurities, and since the absorption observed had not been previously acknowledged, it was important to eliminate or recognise possible contaminants. These could arise either in the original sample during preparation or by the development of a trace of an absorbing species in the pure pyrroline. The various pyrrolines were prepared by quite different routes [15] [(I) by Cloke synthesis; (II) and (III) by the γ-nitroketone route; (IV) by Terentev's method; and (V) and (VI) by the deoxygenation of the corresponding nitrones] and no common impurity is likely. The *N*-oxide is a possible danger in certain examples

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[2] J. W. Sidman, *Chem. Rev.*, 1958, **58**, 689.

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[8] J. Hires and J. Balog, *Acta Phys. et Chem. Szeged.*, 1956, **2**, 87.

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TABLE 1

Ultraviolet absorption of 1-pyrrolines

1-Pyrroline	Ethanol		Hexane	
	$\lambda_{\text{max.}}$	log ε	$\lambda_{\text{max.}}$	log ε
(I) 2-Methyl-	216 *	2·30	227	2·33
(II) 5,5-Dimethyl-	225	2·17	231	2·16
(III) 2,4,4-Trimethyl-	221	2·32	230	2·29
(IV) 2-Isopropyl-3,3-dimethyl-	225	2·22	233	2·16
(V) 3,3,5,5-Tetramethyl-	226	1·92	228 *	2·00
(VI) 2,3,3,5,5-Pentamethyl-	222	2·05	232	2·08
(VII) 2-Phenyl-3,3-dimethyl-	239	3·95	239	4·06

* Band particularly broad; band head indistinct.

[(II), (III), (V) and (VI)] but the observed maxima do not correspond to those of the related nitrones [*e.g.*,[16] 2,4,4-trimethyl-1-pyrroline-1-oxide, $\lambda_{\text{max.}}$ (EtOH) 229 mμ, log ε 3·95; $\lambda_{\text{max.}}$ (hexane) 244 mμ, log ε 4·01; cf. (III)]. Moreover the pyrrolines were carefully purified by fractional distillation and gas–liquid chromatography. Repetition of these processes with 2,4,4-trimethyl-1-pyrroline (III) did not significantly alter the extinction, and it seems unlikely that the absorption is due to an original contaminant.

The 1-pyrrolines are rather unstable, however, since they may promote their own base-catalysed self-condensation: aldol-type condensation is possible in certain instances,[17] and transformation to conjugated azomethines might follow. Reaction is also feasible with carbon dioxide and with oxygen. In the latter case unsaturated amides might reasonably arise *via* pyrroline hydroperoxides.[18] However an α-CH group is required for both aldol condensation and autoxidation, and pyrroline (V) does not contain one. Moreover if the band is due to a transformation product which is slowly generated then the 230 mμ band should intensify with time. This was not observed: the absorption of (III) did not change significantly when the pyrroline was kept overnight either as the pure liquid or in solution at spectroscopic concentration.

Thus the bands described in Table 1 do not appear to be ascribable to impurities. That instrumental characteristics and stray light effects were not important was shown by measuring certain of the spectra on three different recording spectrophotometers, whereupon consistent results were obtained. Moreover the absorption obeyed Beer's law. The evidence below leads to the suggestion that the absorption is due to the $n \rightarrow \pi^*$ transition in the azomethine group and is analogous to the band at ~280 mμ associated with the carbonyl function. (i) The bands are weak, and suffer a bathochromic shift on decreasing the polarity of the solvent[19] (Table 1, Figure 3). (ii) The absorption is missing from solutions of the corresponding pyrrolidines (Figure 2). (iii) Involvement of the non-bonded electrons by protonation causes a reversible change: the weak band is replaced by strong end-absorption (Figure 1) presumably due, in part at least, to the $\pi \rightarrow \pi^*$ band, which also shows a bathochromic shift on protonation of the conjugated azomethine system [*e.g.*, (VII, H^+) $\lambda_{\text{max.}}$ (EtOH) 267 mμ] where the $n \rightarrow \pi^*$ band is normally completely hidden (cf.[20] the conjugated carboxylic acid esters). (iv) Further analogies to the carbonyl chromophore are apparent. Thus aldimines [*e.g.*, (II), (V)] absorb at longer wavelengths than ketimines [*e.g.*, (III), (VI); cf.[21] acetaldehyde, $\lambda_{\text{max.}}$ (hexane) 293·4 mμ; acetone, $\lambda_{\text{max.}}$ (hexane) 279 mμ] while alkylation at carbon atoms adjacent to the unsaturated group has a weak bathochromic effect [cf.[22] hexamethylacetone, $\lambda_{\text{max.}}$ (heptane) 296·8 mμ]. An alkoxy- or

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[16] R. Bonnett, R. F. C. Brown, V. M. Clark, I. O. Sutherland, and Sir Alexander Todd, *J.*, 1959, 2094.

[17] R. Bonnett, V. M. Clark, A. Giddey, and Sir Alexander Todd, *J.*, 1959, 2087.

[18] Cf. L. A. Cohen and B. Witkop, *J. Amer. Chem. Soc.*, 1955, **77**, 6595.

[19] M. Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14; H. McConnell, *J. Chem. Phys.*, 1952, **20**, 700.

[20] W. D. Closson, S. F. Brady, E. M. Kosower, and P. C. Huang, *J. Org. Chem.*, 1963, **28**, 1161.

[21] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, London, 1962.

[22] F. O. Rice, *J. Amer. Chem. Soc.*, 1920, **42**, 727.

hydroxy-substituent at the azomethine group presumably produces a blue shift analogous to that observed in carboxylic acids and esters since no 230 mμ band is observed either in acetoxime [23] or 2-methoxy-1-pyrroline.

The effect of tautomerism remains to be considered. Infrared [17,24] and nuclear magnetic resonance [15] studies have shown that the alkylpyrrolines exist essentially in the azomethine (*i.e.*, 1-pyrroline) form. However if the absorption of secondary enamines is considered to be similar to that of tertiary enamines [*e.g.*,[6] 1-butyl-2-methyl-2-pyrroline, $\lambda_{max.}$ (Et_2O) 238 mμ, log ε 3·86] then a trace of 2-pyrroline, undetectable in the earlier spectral observations, could be responsible for the observed absorption. Clearly in compound (V) this cannot be the explanation, but it is noteworthy that here the extinction is lower than those of the enaminisable pyrrolines, and the *extra* absorption in these cases might be due, in part at least, to the 2-pyrroline tautomer.

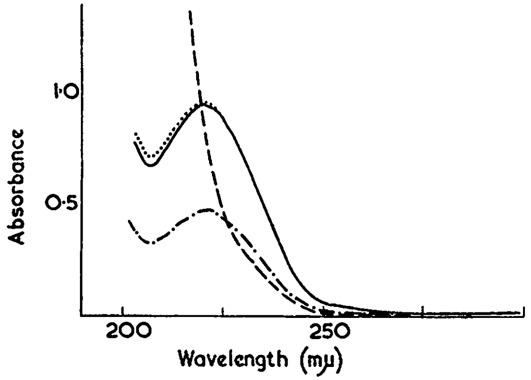

FIGURE 1. Ultraviolet absorption of 2,4,4-trimethyl-1-pyrroline. ——, 13·0 mg. in 25 ml. ethanol; —·—·—, diluted two-fold; — — —, treated with a trace of 6N-HCl; ·····, the acidified solution neutralised with a trace of aqueous ammonia

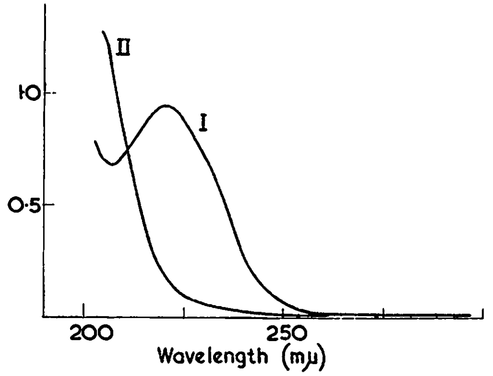

FIGURE 2. Ultraviolet absorption in ethanol. I: 2,4,4-Trimethyl-1-pyrroline (13 mg./25 ml.); II: 2,4,4-Trimethylpyrrolidine (15 mg./25 ml.)

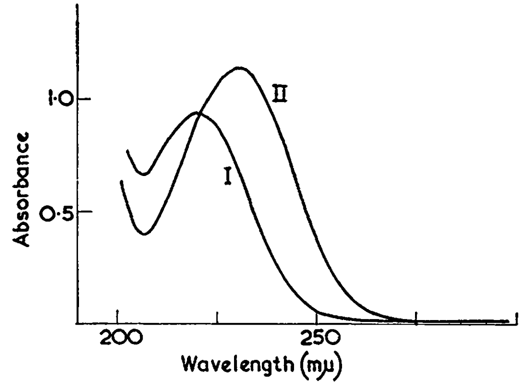

FIGURE 3. Ultraviolet absorption of 2,4,4-trimethyl-1-pyrroline in ethanol (I, 13·0 mg./25 ml.) and in hexane (II, 17·0 mg./25 ml.)

We wished to examine other azomethines in which enaminisation could not occur in order to confirm the important arguments which otherwise depended on one example (V). Neopentylidene derivatives were selected [25] and a convenient preparation employing a

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[23] J. Meisenheimer and O. Dorner, *Annalen*, 1933, **502**, 156.
[24] J. H. Burckhalter and J. H. Short, *J. Org. Chem.*, 1958, **23**, 1278.
[25] R. Bonnett, N. J. David, J. Hamlin, and P. Smith, *Chem. and Ind.*, 1963, 1836.

TABLE 2

Spectral data on *N*-neopentylidene-butylamines

	Azomethine	Ultraviolet (λ, log ε) Ethanol (dry)	Ultraviolet (λ, log ε) Hexane	Infrared (cm.$^{-1}$) ν C=N	Nuclear magnetic resonance (τ) –CH=	Nuclear magnetic resonance (τ) =NCH–	Nuclear magnetic resonance (τ) Bu^t–
(VIII)	*N*-Neopentylidene-n-butylamine	235	244	1665	2·52 *	6·65 *	8·93
	$\mathrm{Me_3C{\cdot}CH{=}NBu}$	(2·03)	(1·94)				
(IX)	*N*-Neopentylidene-s-butylamine	236	243	1665	2·50	7·10	8·95
	$\mathrm{Me_3C{\cdot}CH{=}NCH\ MeEt}$	(1·97)	(1·93)				
(X)	*N*-Neopentylidene-t-butylamine	242	250	1665	2·59	—	8·88
	$\mathrm{Me_3C{\cdot}CH{=}NC\ Me_3}$	(1·92)	(1·90)				8·98

* These signals appear to be weakly coupled ($J \sim 1{\cdot}5$ c./sec.).

molecular sieve was developed. It emerged that these derivatives showed the same type of absorption as the 1-pyrrolines, although the bands of the acyclic compounds were shifted to the red and were somewhat less intense (Table 2). The *N*-neopentylidenealkylamines were colourless fragrant liquids which could be distilled under reduced pressure without apparent decomposition, or purified by preparative vapour phase chromatography. They did not become discoloured on storage, and the absorption of *N*-neopentylidene-n-butylamine was unchanged after several months at 0°. Infrared and nuclear magnetic resonance studies (Table 2) indicated the monomeric formulation. Hydrolysis of *N*-neopentylidene-n-butylamine at spectroscopic concentration in aqueous ethanol appeared to

$$\underset{\lambda_{\max.}\ 234\ \mathrm{m}\mu}{\mathrm{Me_3C{\cdot}CH{=}NC_4H_9}} + \mathrm{H_2O} \rightleftharpoons \underset{\lambda_{\max.}\ 290\ \mathrm{m}\mu}{\mathrm{Me_3C{\cdot}CHO}} + \mathrm{C_4H_9NH_2}$$

give an equilibrium mixture which could be approached from either direction. The effects of solvent polarity and protonation on the absorption band were similar to those observed with the pyrrolines. Since in the neopentylidene derivatives the bands were well removed from the region of end-absorption it was possible to estimate oscillator strengths: thus *N*-neopentylidene-n-butylamine in hexane had $f = 0{\cdot}0011$, a value somewhat greater than that of simple carbonyl compounds, but still of a magnitude characteristic of a forbidden transition.[2]

Clearly these results strengthen the supposition that it is the $n \rightarrow \pi^*$ band that is under observation. Further support comes from optical rotatory dispersion studies in which the first pair of anomalous curves in this series [(+)- and (—)-*N*-neopentylidene-s-butylamine) have now been observed (Figure 4). These show extrema in hexane at about 263 mμ and at about 227 mμ with an amplitude of *ca.* 17. The mid-point lies as expected in the 245 mμ region, *i.e.*, in the region of the observed ultraviolet maximum, and no Cotton effect is observed at higher wavelengths (*i.e.*, no electronic transition of lower energy is detectable). Elsewhere it will be shown that this phenomenon is quite general: azomethines with other asymmetric groups on nitrogen (*e.g.*, amino-acid derivatives[26]) or with asymmetry in the alkylidene group (*e.g.*, steroidal azomethines[27]) give similar Cotton effect curves even though the azomethine band itself, being weak and easily submerged in background absorption, cannot always be distinguished in the ultraviolet absorption spectrum. Evidently the 235 mμ band is " optically active " and this observation, together with the previous evidence, strongly support the proposition that it is due to the $n \rightarrow \pi^*$ transition of the azomethine group.

Because of its proximity to the edge of the quartz region the azomethine band is unlikely to prove as valuable in structural work as the carbonyl absorption. Nevertheless it does appear to be suitable for the kinetic study of the hydrolysis of aliphatic azomethines and, in optical rotatory dispersion work, it offers a notable advantage over the carbonyl

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[26] Z. Badr, R. Bonnett, T. R. Emerson, and W. Klyne, unpublished results.
[27] R. Bonnett and T. R. Emerson, unpublished results.

group in that the effect of substituents in the " front octants " can, in principle, be readily observed. A further interest lies in the photochemistry of the azomethine group, and exploratory studies in this area have now begun.

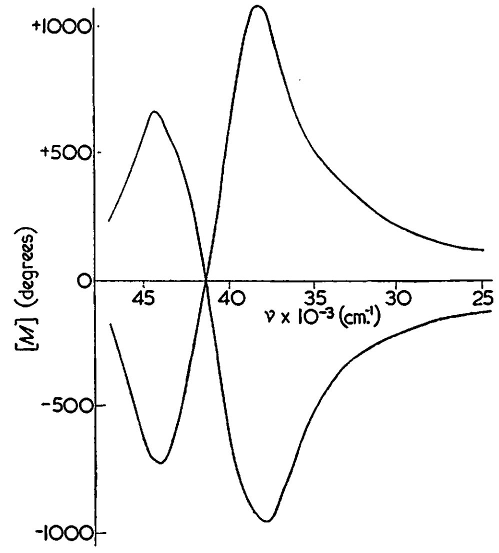

FIGURE 4. Optical rotatory dispersion of (+) and (−)-*N*-neopentylidene-s-butylamine in hexane

EXPERIMENTAL

Ultraviolet spectra were measured on both the Cary 11 and Unicam S.P. 700 spectrophotometers: in some cases measurements were also made on the Unicam S.P. 800 B spectrophotometer. The solvents used were 95% ethanol and hexane (" Special for spectroscopy," British Drug Houses, Ltd.). The samples were weighed in capillaries: reproducibility of wavelengths 1 mμ; of extinctions $\sim$10%. Infrared spectra were measured as films on a Unicam S.P. 200 instrument. Nuclear magnetic resonance spectra (Varian A60 instrument) were observed in $[^2H]$chloroform using internal tetramethylsilane as reference. Calibrations for the three types of spectrum was carried out using a holmium filter, a polystyrene film, and an appropriate side band ($\sim$500 c./sec.) respectively. The pyrrolines were prepared as previously indicated [15] except for compounds (V) and (VI) which were made by the deoxygenation of the corresponding nitrones.[28]

Effect on the Ultraviolet Absorption of 2,4,4-*Trimethyl*-1-*pyrroline of Storage of the Sample.*—A sample of 2,4,4-trimethyl-1-pyrroline purified by gas–liquid chromatography (5 ft. Ucon polar column at 120°, helium carrier, retention volume 205 ml.) had $\lambda_{max.}$ (EtOH) 221 mμ, ε 225. After short-path distillation $\lambda_{max.}$ (EtOH) 221 mμ, ε 215, 210 was observed, and this absorption did not change on keeping the solution overnight. On keeping the *liquid* in a stoppered vessel at room temperature the following extinctions were observed in ethanol: overnight: 212, 213; after three days, when the pyrroline had become faintly yellow: 230, 218.

N-*Neopentylidene Derivatives.—General method.* Pivaldehyde (freshly-distilled, 1—2 g.) was treated with a slight excess of the dry, freshly-distilled butylamine. With n-butylamine the mixture became hot and cloudy almost at once; with s-butylamine there was a delay ($\sim$2 min.), and with t-butylamine the mixture did not become warm and the cloudiness took $\sim$20 min. to develop. In all cases water separated as a lower layer: this was removed with a capillary dropper and the reaction was driven to completion with molecular sieve (Linde 4A, 0·5 g., overnight). Distillation gave the *N*-neopentylidene alkylamines which could be further purified by gas–liquid chromatography (conditions as above); N-*neopentylidene-n-butylamine*, 70%, b. p. 94°/150 mm.; 142—143°/750 mm. (lit.,[29] 145—146°); retention volume 320 ml. (Found: C, 76·3; H, 13·65; N, 10·0. $C_9H_{19}N$ requires C, 76·5; H, 13·6; N, 9·9%);

[28] R. Bonnett and G. F. Stephenson, unpublished work.

[29] A. Schellenberger, G. Osske, and W. Rodel, *Z. physiol. Chem.*, 1962, **329**, 149.

warming with Brady's reagent precipitated pivaldehyde 2,4-dinitrophenylhydrazone; N-*neopentylidene-s-butylamine*, 50%, b. p. 70—71°/100 mm.; retention volume 180 ml. [Found (on sample from (−)-s-butylamine [30]): C, 76·7; H, 13·5; N, 10·1%]; azomethine from (−)-s-butylamine: RD in hexane (*c* 0·28): $[M]_{100}$ −100°, $[M]_{264}$ −930°, $[M]_{242}$ 0°, $[M]_{226}$ +655°, $[M]_{213}$ +235°; Azomethine from (+)-s-butylamine: RD in hexane (*c* 0·23): $[M]_{400}$ +130°, $[M]_{262}$ +1100°, $[M]_{243}$ 0°, $[M]_{228}$ −740°, $[M]_{213}$ −185°; *N-neopentylidene-t-butylamine*, 52%, b. p. 74°/150 mm., retention volume 94 ml. (Found: C, 75·9; H, 13·4; N, 10·5%). This azomethine deposited white needles (t-butylammonium pivalate) unless kept in a sealed tube: this salt did not have an absorption band at ~230 mμ. Spectral data for these azomethines are recorded in Table 2.

Some early experiments were carried out by N. J. David, J. Hamlin, and P. Smith. Professor W. Klyne and Mr. John Jennings are thanked for the O.R.D. measurements and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a research grant. The Royal Society is thanked for a grant for the purchase of an ultraviolet spectrophotometer.

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[30] P. Bruck, I. N. Denton, and A. H. Lamberton, *J.*, 1956, 921.