# **908.** *Heterocyclic Systems Related to Pyrrocoline. Part III.*[1] *The Ultraviolet Absorption of Some Polyazaindenes.*

By J. D. Bower.

An improved synthesis of 1 : 3*a*-diazaindene (pyrimidazole) is described. The ultraviolet absorption spectra of the polyazaindene systems having the nitrogen atoms in the five-membered ring are recorded and compared.

THE preparation of several new polyazaindene systems was described in Parts I and II.[1] Spectroscopic confirmation of their structures is now presented. For this purpose the other polyazaindenes having the nitrogen atoms only in the five-membered ring have been prepared and the ultraviolet absorption spectra of all the systems have been examined. In general, standard methods were used for the preparation of the known compounds.

Kröhnke and his co-workers [2] recently reported investigations of routes to derivatives of 1 : 3*a*-diazaindene (pyrimidazole), but the only preparation of the parent member (I; R = H) so far is that by Tschitschibabin [3] who prepared it from bromoacetaldehyde and 2-aminopyridine in unstated yield. This compound is conveniently prepared by dehydrogenation of the readily available 2 : 3-dihydro-1 : 3*a*-diazaindene [4] by potassium ferricyanide or lead tetra-acetate.

1 : 2 : 3*a*-Triazaindene (II; R = H) was prepared by a slight modification of the published method,[5] and the 3-methyl derivative (II; R = Me) was also obtained. The hygroscopic nature of the former was confirmed, and the latter readily forms a hydrate.

Details of the ultraviolet absorption spectra (*cyclo*hexane solutions) of the parent

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[1] Part I, Bower and Ramage, *J.*, 1955, 2834; Part II, *idem*, preceding paper.

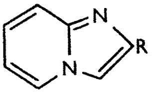
[2] Schilling, Kröhnke, and Kickhöfen, *Chem. Ber.*, 1955, **88**, 1093; Kröhnke and Kickhöfen, *ibid.*, p. 1103.

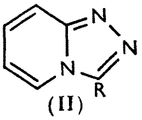
[3] Tschitschibabin, *Ber.*, 1925, **58**, 1704.

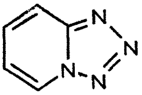
[4] Bremer, *Annalen*, 1936, **521**, 286.

[5] Fargher and Furness, *J.*, 1915, 688.

members of six of the seven polyazaindenes having the nitrogen atoms in the five-membered ring are given in the Table and Figures. The exception, 1 : 3 : 3*a*-triazaindene, has not yet been prepared, but details of the spectrum of its 2-methyl derivative are given. Since, in general, the presence of a *C*-methyl substituent has little effect on the spectrum of a heterocyclic compound,[6] it is considered justifiable to regard the spectrum of 2-methyl-1 : 3 : 3*a*-triazaindene as being very similar to that of the parent in a comparative study of the forms of the spectra of the systems. The spectra of some phenylpolyazaindenes are also recorded.


(I)


(II)


(III)

Consideration of the compounds as derived from pyrrocoline shows a clear connection between the spectra and the number and positions of the nitrogen atoms. The spectrum of pyrrocoline (Fig. 1) consists of three absorption bands, the two at longer wavelengths showing characteristic fine structure. Replacement of the ‒CH= group in the 2-position by nitrogen, to give 2 : 3*a*-diazaindene (Fig. 1) causes a slight hypsochromic shift, but in the 1- or 3-position the effect, especially on the longest-wavelength band, is considerably

*Ultraviolet absorption spectra.*

| Compound | M. p. | Concn. (10⁻⁵M) | Absorption max. (Å) and log ε (in parentheses) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Pyrrocoline [a] | 74° | 2·08 | 3815<br>(2·92) | 3610<br>(3·24) | 3465<br>(3·29) | 3360 *<br>(3·23) | 2945<br>(3·56) | 2825<br>(3·45) | 2755<br>(3·34) | | 2375<br>(4·51) |
| 1 : 3*a*-Diazaindene [b] | (109°/2 mm.†) | 3·40 | 3360<br>(3·10) | 3200<br>(3·38) | 3100<br>(3·42) | | 2800<br>(3·41) | 2725<br>(3·38) | 2530 *<br>(3·15) | 2285 *<br>(4·29) | 2245<br>(4·41) |
| 2 : 3*a*-Diazaindene [c] | 54—55° | 3·40 | 3785<br>(2·89) | 3580<br>(3·20) | 3440<br>(3·27) | 3330 *<br>(3·23) | 2845<br>(3·66) | 2735<br>(3·72) | 2650 *<br>(3·55) | | 2180<br>(4·46) |
| 1 : 7*a*-Diazaindene [d] | (108°/ 25 mm.†) | 3·22 | 3400<br>(2·72) | 3230 *<br>(3·14) | 3100<br>(3·25) | 3005 *<br>(3·26) | 2890<br>(3·52) | 2810 *<br>(3·46) | | 2270<br>(4·54) | 2225<br>(4·56) |
| 1 : 2 : 3*a*-Triaza-indene (hydrate) [b] | 36° | 3·27 | 3260<br>(2·93) | 3110<br>(3·28) | 2990<br>(3·36) | 2930 *<br>(3·34) | 2700<br>(3·33) | 2595<br>(3·32) | | | 2140<br>(4·35) |
| 2-Methyl-1 : 3 : 3*a*-triazaindene [d] ...... | 49—50° | 3·19 | 2940 *<br>(3·20) | 2810 *<br>(3·52) | | | 2730<br>(3·57) | | | | 2175<br>(4·58) |
| 1 : 2 : 7*a*-Triaza-indene [d] | 39—40° | 3·17 | 3355<br>(2·85) | 3190 *<br>(3·25) | 3060<br>(3·34) | 3000<br>(3·33) | 2835<br>(3·66) | 2740<br>(3·67) | | | 2130<br>(4·38) |
| 1 : 2 : 3 : 3*a*-Tetra-azaindene [e] | 157° | 3·50 | 2930<br>(3·16) | 2805<br>(3·47) | | | 2685 *<br>(3·61) | 2645<br>(3·62) | | | <2100 |
| 2-Phenylpyrroc-oline [f] | 214° | 1·97 | 3845<br>(3·15) | 3660<br>(3·43) | 3500<br>(3·45) | 3250 *<br>(3·27) | | | 2545<br>(4·62) | | |
| 2-Phenyl-1 : 3*a*-diazaindene [g] | 136° | 1·82 | 3480<br>(3·67 | 3325<br>(3·88) | 3200<br>(3·85) | | 2950<br>(3·66) | 2830<br>(3·69) | 2480<br>(4·62) | | |
| 2-Phenyl-1 : 7*a*-diazaindene [d] | 109° | 1·87 | 3430<br>(2·80) | 3260 *<br>(3·26) | | | 2685<br>(4·49) | 2590<br>(4·56) | 2440<br>(4·53) | | |
| 2-Phenyl-1 : 3 : 3*a*-triazaindene [d] | 141° | 1·77 | 3060<br>(3·58) | 2925 *<br>(3·73) | 2810 *<br>(3·88) | | | 2525<br>(4·56) | 2445<br>(4·56) | | |
| 3-Phenyl-2 : 3*a*-diazaindene [c] | 109° | 1·46 | | 3180<br>(4·11) | | | | 2285<br>(4·22) | | | |
| 3-Phenyl-1 : 2 : 3*a*-triazaindene [h] | 176° | 2·54 | | 2875<br>(3·97) | | | 2430<br>(4·16) | 2210<br>(4·23) | | | |

* Inflexion. † B. p.

Preparations: [a] By decarboxylation (Diels *et al.*, *Annalen*, 1932, **498**, 16) of pyrrocoline-2-carboxylic acid (Borrows and Holland, *J.*, 1947, 672). [b] See Experimental. [c] Part 1. [d] Preceding paper. [e] Ref. 5. [f] Borrows, Holland, and Kenyon, *J.*, 1946, 1069. [g] Ref. 8. [h] Bower and Doyle, *J.*, 1957, 727.

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[6] See, *e.g.*, Ames, Bowman, and Grey, *J.*, 1953, 3008; Cookson, *ibid.*, p. 2789; Passerini, *J.*, 1954, 2256.

greater. The effect is cumulative with the introduction of further nitrogen atoms and results in the merging of the two long-wavelength bands into one in the spectrum of 1 : 2 : 3 : 3*a*-tetra-azaindene [5] (III) (Fig. 1), though some fine structure, characteristic of the long-wavelength band, is still visible.

In the spectra of 2- and 3-phenylpolyazaindenes (Fig. 2) the effects of introducing nitrogen are similar to those for parent compounds.

The relations between the spectra, reflecting the differences between the compounds in the number and position of the nitrogen atoms, are regarded as supporting the assignment, in Parts I and II, of structures to those polyazaindenes not previously described.

The spectra of the phenylpolyazaindenes provide further evidence about the structure of the compound, m. p. 135—136°, obtained from the reaction of 2-aminopyridine with ω-bromoacetophenone. Tschitschibabin [7] and Schmid and Bangler [8] regarded this as 2-phenyl-1 : 3*a*-diazaindene (though without conclusive evidence), but Djerassi and Pettit [9] favoured the 3-phenyl structure. Recently Kröhnke, Kickhöfen, and Thoma [10] have shown that the compound is, in fact, the 2-phenyl isomer (I; R = Ph) and this is supported by the spectrum (Fig. 2), which is of the same type as those of 2-phenylpyrrocoline and 2-phenyl-1 : 3 : 3*a*-triazaindene but distinct from those of 3-phenyl-2 : 3*a*-diazaindene and 3-phenyl-1 : 2 : 3*a*-triazaindene. An isomer, m. p. 98°, considered to be 3-phenyl-1 : 3*a*-diazaindene has been described.[11]

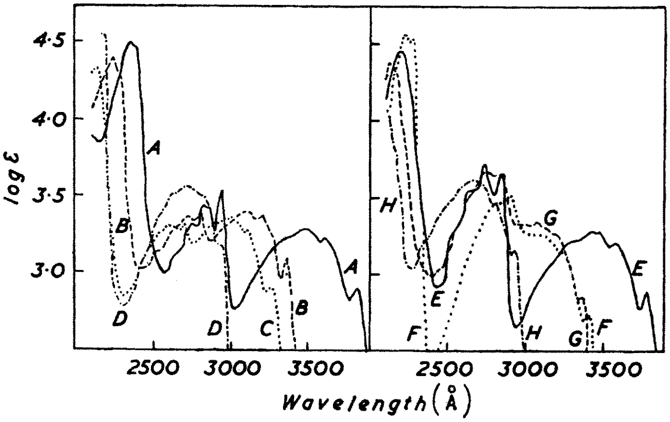

FIG. 1.

*A*, *Pyrrocoline*. *B*, 1 : 3a-*Diazaindene*. *C*, 1 : 2 : 3a-*Triazaindene hydrate*. *D*, 2-*Methyl*-1 : 3 : 3a-*triazaindene*. *E*, 2 : 3a-*Diazaindene*. *F*, 1 : 7a-*Diazaindene*. *G*, 1 : 2 : 7a-*Triazaindene*. *H*, 1 : 2 : 3 : 3a-*Tetra-azaindene*.

## EXPERIMENTAL

*Absorption Spectra*.—These were determined in *cyclo*hexane solution (for concentrations see Table) on a Unicam S.P. 500 spectrophotometer. 1 cm. and 4 cm. cells were used.

1 : 3a-*Diazaindene* (*Pyrimidazole*) (I; R = H).—(*a*) 2 : 3-Dihydro-1 : 3*a*-diazaindene [4] (4·65 g.), potassium ferricyanide (31·9 g.), and sodium hydrogen carbonate (8·2 g.) were heated in water (125 c.c.) at 90—100° for 30 min. Addition of 30% sodium hydroxide solution (25 c.c.), extraction with chloroform, and distillation of the dried ($Na_2SO_4$) extract gave a yellow oil (3·63 g., 79%), b. p. 114—115°/3 mm. The colour was removed by the passage of the oil, in benzene containing 1% by volume of ethanol, through a column of alumina, and 1 : 3*a*-diazaindene (2·76 g., 60%), b. p. 109°/2 mm., was obtained on distillation of the eluate (Found: C, 71·2; H, 5·1. Calc. for $C_7H_6N_2$: C, 71·2; H, 5·1%). It showed a blue fluorescence under ultraviolet light. The *picrate* formed fine needles, m. p. 205°, from ethanol (Found: C, 45·4;

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[7] Tschitschibabin, *Ber.*, 1926, **59**, 2048.
[8] Schmid and Bangler, *ibid.*, p. 1360.
[9] Djerassi and Pettit, *J. Amer. Chem. Soc.*, 1954, **76**, 4470.
[10] Kröhnke, Kickhöfen, and Thoma, *Chem. Ber.*, 1955, **88**, 1117.
[11] Gol'dfarb and Kondakova, *J. Appl. Chem. U.S.S.R.*, 1942, **15**, 151.

H, 2·9. $C_7H_6N_2,C_6H_3O_7N_3$ requires C, 45·0; H, 2·6%), and the *methiodide* fine needles, m. p. 207°, from propanol (Found: C, 37·1; H, 3·7. $C_8H_9N_2I$ requires C, 36·9; H, 3·5%).

(*b*) Lead tetra-acetate (4·5 g.) was added to 2 : 3-dihydro-1 : 3*a*-diazaindene (1·2 g.) in benzene (50 c.c.). After complete reaction the mixture was filtered, the filtrate washed with 30% sodium hydroxide solution, and the benzene layer fractionated to give 1 : 3*a*-diazaindene (0·56 g., 47%), b. p. 115°/3 mm. The picrate was identical with that obtained by method (*a*).

1 : 2 : 3a-*Triazaindene* (II; R = H).—The procedure used was that of Fargher and Furness,[5] except that the distillation was continued after the removal of the excess of formic acid and the triazaindene (81%) was obtained as a liquid, b. p. 218°/6 mm., which formed a deliquescent solid. Crystallisation from moist benzene or moist ethyl acetate gave the *hydrate* as needles, m. p. 36° (Found: C, 52·4; H, 5·0. $C_6H_5N_3,H_2O$ requires C, 52·5; H, 5·1%).

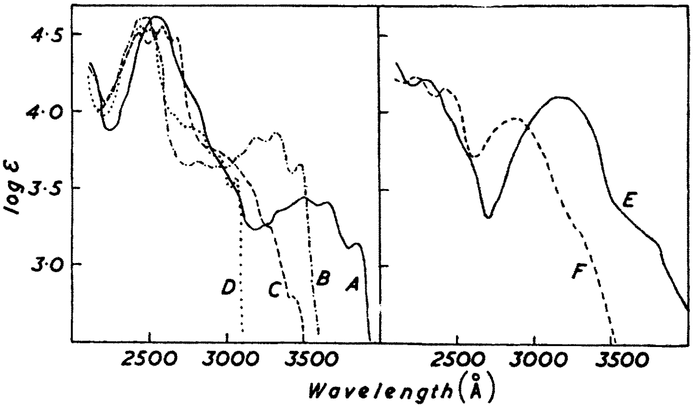

FIG. 2.

*A*, *2-Phenylpyrrocoline.* *B*, *2-Phenyl-*1 : 3a-*diazaindene.* *C*, 2-*Phenyl*-1 : 7a-*diazaindene.* *D*, *2-Phenyl*-1 : 3 : 3a-*triazaindene.* *E*, *3-Phenyl*-2 : 3a-*diazaindene.* *F*, *3-Phenyl*-1 : 2 : 3a-*triazaindene.*

Although the hydrate could be partly dehydrated over phosphoric oxide an anhydrous sample was not obtained.

3-*Methyl*-1 : 2 : 3a-*triazaindene* (II; R = Me).—2-Pyridylhydrazine (2·0 g.) was boiled in acetic anhydride (4 c.c.) for 5 hr. The excess of solvent was removed under reduced pressure and the residue was treated with 30% sodium hydroxide solution (20 c.c.). The resulting solid was extracted with chloroform, the extract evaporated, and the residue crystallised from benzene to give 3-*methyl*-1 : 2 : 3a-*triazaindene* as prisms, m. p. 134° (Found: C, 62·5; H, 5·3. $C_7H_7N_3$ requires C, 63·1; H, 5·3%). The *trihydrate* formed needles, m. p. 56°, from water or moist ethyl acetate (Found: C, 45·6; H, 7·1. $C_7H_7N_3,3H_2O$ requires C, 44·9; H, 7·0%). The *picrate* formed prisms, m. p. 239—241°, from acetone (Found: C, 43·1; H, 3·1. $C_7H_7N_3,C_6H_3O_7N_3$ requires C, 43·1; H, 2·8%). The *methiodide*, obtained as needles, m. p. 243—244°, from acetone (Found: C, 34·8; H, 3·9. $C_8H_{10}N_3I$ requires C, 34·9; H, 3·7%), when boiled with *p*-dimethylaminobenzaldehyde in methanol containing a little piperidine, formed 3-p-*dimethylaminostyryl-2-methyl*-1 : 2 : 3a-*triazaindene iodide*, which crystallised from methanol as fine orange needles, m. p. 269° (Found: C, 50·3; H, 4·6. $C_{17}H_{19}N_4I$ requires C, 50·4; H, 4·7%), $\lambda_{max.}$ 4220 Å (ε 35,800; $1·1 \times 10^{-5}$M in MeOH).

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