610. *Quinoxaline Analogues. Part VII.*[1] *Derivatives of 1,4,6-Triazanaphthalene.*

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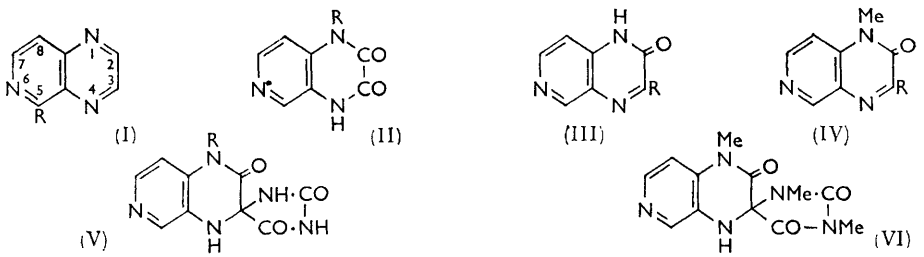
1,4,6-Triazanaphthalene analogues of previously described quinoxaline-[2] and 1,4,5-triazanaphthalene-carboxyureides [3] and -spirohydantoins, and other derivatives, have been prepared by condensing 3,4-diaminopyridines with 1,2-dicarbonyl compounds.

Among the triazanaphthalenes the 1,4,5- and the 1,4,6-triaza-compound are especially interesting because they are isosteric with pteridine and can be regarded as 3-deazapteridine and 1-deazapteridine (I; R = H), respectively. Derivatives of 1,4,5-triazanaphthalene were described earlier [3] and corresponding 1,4,6-triazanaphthalene derivatives are now reported. The parent 1,4,6-triazanaphthalene (I; R = H) was prepared by Koenigs *et al.*[4] who also obtained 5-chloro-1,4,6-triazanaphthalene but described it as 7-chloro-1,4,6-triazanaphthalene because they regarded 3,4-diamino-2-chloropyridine [5] as the



6-chloro-compound. 5-Amino- and 5-hydroxy-1,4,6-triazanaphthalene (I; R = NH_2, OH) were prepared [6] much later and the only other derivatives of the ring system known at the beginning of the present investigation in 1959 were a phenanthro-fused system [4] and two compounds (II; R = Ph and Bu^n) prepared [7] from ethyl oxalate and the appropriate diaminopyridines. The lability [8] of 1,4,6-triazanaphthalene is now known to be due to reversible covalent hydration of the 1,2-bond rather than ring fission.[9] 8-Nitro- and 8-amino-2,3-dimethyl-1,4,6-triazanaphthalene, 8-amino-1,4,6-triazanaphthalene, and 8-amino-2(and 3)-methyl-1,4,6-triazanaphthalene were described [10] while our work was in progress, and also 2,3-dimethyl-1,4,6-triazanaphthalene and its 1,2,3,4-tetrahydro-derivative.[11]

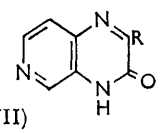
The most obvious route to 1,4,6-triazanaphthalenes is by condensation of 3,4-diaminopyridines with 1,2-dicarbonyl compounds, and all thirteen known derivatives have been prepared by this method, sometimes with subsequent modification of a substituent. 3,4-Diamino- and 4-alkylamino-3-amino-pyridines are easily prepared, and 3-alkylamino-4-aminopyridines are available in a four-stage synthesis from 3-bromopyridine.[12] 3,4-Diamino- and 2-chloro-3,4-diamino-pyridine were converted into 1,4,6-triazanaphthalene

[1] Part VI, Clark-Lewis and Katekar, *J.*, 1959, 2825.
[2] Clark-Lewis, *J.*, 1957, 422.
[3] Clark-Lewis and Thompson, *J.*, 1957, 430.
[4] Koenigs, Bueren, and Jung, *Ber.*, 1936, **69**, 2690.
[5] Talik and Plazek, *Roczniki Chem.*, 1956, **30**, 1139.
[6] Albert and Hampton, *J.*, 1952, 4985.
[7] Bremer, *Annalen*, 1937, **529**, 290.
[8] Albert and Pedersen, *J.*, 1956, 4683.
[9] Personal communication from Professor A. Albert.
[10] Israel and Day, *J. Org. Chem.*, 1959, **24**, 1455.
[11] De Selms and Mosher, *J. Amer. Chem. Soc.*, 1960, **82**, 3762.
[12] Clark-Lewis and Singh, *J.*, 1962, 2379.

(I; R = H) and its 5-chloro-derivative (I; R = Cl) with glyoxal sodium bisulphite compound, and hydrogenolysis of the chloro-compound over palladium also gave 1,4,6-triazanaphthalene. Condensation of 3,4-diaminopyridine with biacetyl and with benzil gave 2,3-dimethyl-[11] and 2,3-diphenyl-1,4,6-triazanaphthalene; the former is remarkable for the deep blue colour it gives immediately on the addition of concentrated hydrochloric acid.

When 3,4-diaminopyridine was condensed with unsymmetrical dicarbonyl compounds (ethyl pyruvate, ethyl mesoxalate, alloxan) the products contained a 2- or a 3-carbonyl group, and the orientation was confirmed by conversion into the *N*-methyl derivatives. Ethyl pyruvate and 3,4-diaminopyridine gave a mixture from which 2-hydroxy-3-methyl-1,4,6-triazanaphthalene (III; R = Me) was obtained, and this was converted by diazomethane into 1,2-dihydro-1,3-dimethyl-2-oxo-1,4,6-triazanaphthalene (IV; R = Me), identical with that prepared from 3-amino-4-methylaminopyridine.

Alloxan and 3,4-diaminopyridine gave 2-hydroxy-1,4,6-triazanaphthalene-3-carboxyureide (III; R = CO·NH·CO·NH_2), which readily cyclised in hot acetic acid to the spiran (V; R = H), this reaction being analogous to the cyclisation of the 1,4,5-triazanaphthalenecarboxyureides.[3] 3-Amino-4-methylaminopyridine and alloxan gave a spiran (V; R = Me) directly owing to ready cyclisation of the intermediate ureide. Ethereal diazomethane converted the spiran (V; R = Me) into the trimethyl-spiran (VI), and the orientation of compound (V; R = H) was confirmed by its conversion with ethereal diazomethane into the same product (VI). 1,2,3,4-Tetrahydro-4-methyl-3-oxo-1,4,6-triazanaphthalene-2-spiro-5′-hydantoin was prepared from 4-amino-3-methylaminopyridine for comparison with the isomer (V; R = Me).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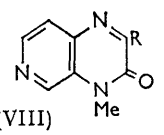
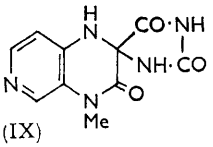

(VIII)


(IX)

Hydrolysis of the ureides or the spirohydantoins gave the corresponding triazanaphthalenecarboxylic acids, and specimens of these acids were therefore required for comparison. Condensing 3,4-diaminopyridine with ethyl mesoxalate gave a mixture of esters (III and

Light absorption of 1,4,6-triazanaphthalenes in 95% ethanol. Wavelength (mμ) of maximum absorption (ε in parentheses).

Dihydro-oxo-1,4,6-triazanaphthalenes.			
IV; R = H	236 (26,700)	—	315 (7500)
VIII; R = H	234 (27,000)	—	312 (7450)
III; R = Me	232 (24,000)	—	305 (7000)
IV; R = Me	236 (24,300)	250 * (6750)	307 (7000)
VIII; R = Me	230 (24,000)	—	343 (5600)
III; R = CO_2Et	229 (15,000)	250 (10,000)	359—360 (3500)
VII; R = CO_2Et		250 (18,200)	343 (5800)
IV; R = CO_2Et	238 (27,800)	293 (6100)	326 (5500)
VIII; R = CO_2Et	237 (28,000)	292 (5900)	319 (5400)
III; R = CO_2H	224 (16,700)	275 (2500)	368 (7600)
IV; R = CO_2H	234 (23,500)	268 (2800)	328—332 (6200)
VIII; R = CO_2H	228 (21,800)	270 (2500)	321 (4500)
III; R = $CO·NH_2$	229 (19,900)	286 (5400)	386 (7500)
IV; R = $CO·NH_2$	238 (24,900)	294 (6000)	331—336 (5500)
VIII; R = $CO·NH_2$	236 (24,700)	290—292 (6000)	328 (4800)
III; R = CO·NH·$CO·NH_2$	230 (22,600)	286 (5000)	371 (8000)
Tetrahydro-oxo-1,4,6-triazanaphthalenes.			
IX	222 (20,900)	—	306 (4200)
V; R = H	225 (21,700)	—	308 (4200)
V; R = Me	220 (21,600)	—	309 (3800)
VI	225 (25,400)	—	310 (4000)

* Inflexion.

VII; R = CO_2Et) which were separated by fractional crystallisation. With diazomethane these gave the methylated esters (IV and VIII; R = CO_2Et) identical with specimens prepared by reaction of ethyl mesoxalate with 3-amino-4- and 4-amino-3-methylaminopyridine. Ammonolysis of the corresponding esters gave the amides (III, IV, VII, and VIII; R = $CO{\cdot}NH_2$). Hydrolysis of the esters gave the acids (IV and VIII; R = CO_2H), which on decarboxylation gave 1,2-dihydro-1-methyl-2-oxo- (IV; R = H) and 3,4-dihydro-4-methyl-3-oxo-1,4,6-triazanaphthalene (VIII; R = H).

The light absorption of 1,4,6-triazanaphthalene was similar to that of quinoxaline,[13] and the light absorption characteristics of analogous quinoxaline and 1,4,6-triazanaphthalene derivatives were also very similar. Ultraviolet light absorption measurements provided the most convenient distinction between the dihydro- and tetrahydro-1,4,6-triazanaphthalene derivatives (see Table) as noted with the quinoxaline [2] and 1,4,5-triazanaphthalene analogues.[3] 1,4,6-Triazanaphthalene derivatives were generally similar to their 1,4,5-triazanaphthalene analogues in chemical properties.

Experimental

Unless otherwise stated, compounds were dissolved in 95% ethanol for measurement of light absorption.

1,4,6-Triazanaphthalene, m. p. 98° (lit.,[8] m. p. 97°) was prepared from 3,4-diaminopyridine [12] and glyoxal monohydrate, and purified by elution from alumina with light petroleum (b. p. 60—80°). It had $\lambda_{max.}$ 232 (ε 25,400) and 309 (ε 4500), $\lambda_{min.}$ 212 (ε 5450); $\lambda_{infl.}$ 252—282 mμ (ε 2300). It had a characteristic mouse-like odour and became brown on exposure to air.

5-Chloro-1,4,6-triazanaphthalene was obtained (66%) from 2-chloro-3,4-diaminopyridine [5,14] and glyoxal sodium bisulphite compound; it crystallised from light petroleum (b. p. 80—100°) in needles, m. p. 139—140°. The compound has been described as 7-chloro-1,4,6-triazanaphthalene.[4] Hydrogenation in 0·5N-sodium hydroxide over 5% palladised calcium carbonate converted the chloro-compound into 1,4,6-triazanaphthalene (50%), m. p. and mixed m. p. 98°.

2,3-*Dimethyl*-1,4,6-*triazanaphthalene*.—3,4-Diaminopyridine (3 g.) and butane-2,3-dione (2·5 g.) were boiled with ethanol (130 c.c.) under reflux for 2 hr. The solution was evaporated and the residue was purified by dissolution in light petroleum (b. p. 60—80°) and chromatography on alumina. Elution with benzene–light petroleum (1 : 1) gave 2,3-dimethyl-1,4,6-triazanaphthalene (3·47 g., 79%), which crystallised from light petroleum (b. p. 100—120°) in plates, m. p. 126° (Found: C, 67·9; H, 5·7; N, 26·1. Calc. for $C_9H_9N_3$: C, 67·9; H, 5·7; N, 26·4%). The compound had a characteristic mouse-like odour and became brown on exposure to air and light, gave a deep blue solution in concentrated hydrochloric acid, and had $\lambda_{max.}$ (in water) 232—234 (ε 27,400) and 312 (ε 5100), $\lambda_{min.}$ 219 (ε 9700) and 270—274 mμ (ε 2700).

2,3-*Diphenyl*-1,4,6-*triazanaphthalene*.—3,4-Diaminopyridine (4 g.), benzil (8 g.), and ethanol (250 c.c.) were boiled for 1 hr. under reflux and the solution was kept at 0° for 24 hr. Filtration gave 2,3-*diphenyl*-1,4,6-*triazanaphthalene* which crystallised from aqueous ethanol (charcoal) in needles (6·25 g., 60%), m. p. 177° (Found: C, 80·5; H, 4·8; N, 14·7. $C_{19}H_{13}N_3$ requires C, 80·5; H, 4·6; N, 14·8%), $\lambda_{max.}$ 234 (ε 33,400), 264—266 (ε 19,400), and 345—346 (ε 10,600), $\lambda_{min.}$ 254 (ε 18,500) and 314 mμ (ε 6200). The compound gave a yellow solution in concentrated hydrochloric acid.

2-*Hydroxy*-3-*methyl*-1,4,6-*triazanaphthalene* (III; R = Me).—3,4-Diaminopyridine (1·4 g.) in ethanol (50 c.c.) was heated under reflux for 1 hr. with ethyl pyruvate (1·6 g.), and the solution was then kept at 0° for 4 hr. Filtration gave a crystalline mixture from which 2-*hydroxy*-3-*methyl*-1,4,6-*triazanaphthalene* (1·03 g., 50%) was extracted with benzene (Soxhlet); this crystallised from ethanol–benzene (charcoal) in yellow needles, m. p. 276—278° (decomp.) (Found: C, 59·7; H, 4·5; N, 26·2. $C_8H_7N_3O$ requires C, 59·6; H, 4·4; N, 26·1%). The solid which remained undissolved in the benzene (Soxhlet) crystallised from aqueous ethanol (charcoal) in colourless needles (0·45 g., 22%), m. p. 262—263° (decomp.) (Found: C, 58·8; H, 4·6; N, 25·0%), apparently consisting of impure 3-hydroxy-2-methyl-1,4,6-triazanaphthalene.

[13] Bohlmann, *Chem. Ber.*, 1951, **84**, 860.
[14] Bremer, *Annalen*, 1935, **518**, 274.

1,2-Dihydro-1,3-dimethyl-2-oxo-1,4,6-triazanaphthalene (IV; R = Me).—3-Amino-4-methylaminopyridine [12] (2 g.), ethyl pyruvate (2·5 g.), and ethanol (100 c.c.) were heated under reflux for 1½ hr. and the solvent was evaporated under reduced pressure. Crystallisation of the residue from aqueous ethanol (charcoal) gave *1,2-dihydro-1,3-dimethyl-2-oxo-1,4,6-triazanaphthalene* (2·6 g., 90%) in needles, m. p. 276—277° (Found: C, 61·5; H, 5·1; N, 23·9. $C_9H_9N_3O$ requires C, 61·7; H, 5·2; N, 24·0%). The compound was also obtained (20%) from 2-hydroxy-3-methyl-1,4,6-triazanaphthalene and diazomethane.

3,4-Dihydro-2,4-dimethyl-3-oxo-1,4,6-triazanaphthalene (VIII; R = Me).—4-Amino-3-methylaminopyridine [12] (0·4 g.) in benzene (25 c.c.) was heated under reflux with ethyl pyruvate under nitrogen for 4 hr. and water was then removed by azeotropic distillation. Heating was continued for 4 hr. and the product was collected from the cooled solution; recrystallisation from ethanol–hexane (charcoal) gave *3,4-dihydro-2,4-dimethyl-3-oxo-1,4,6-triazanaphthalene* (0·3 g., 53%), in pale yellow needles, m. p. 228—230° (decomp.) (Found: C, 61·4; H, 5·25; N, 23·8. $C_9H_9N_3O$ requires C, 61·7; H, 5·2; N, 24·0). The compound was also obtained (26%) by methylation with diazomethane of the impure 3-hydroxy-2-methyl-1,4,6-triazanaphthalene described above.

2-Hydroxy-1,4,6-triazanaphthalene-3-carboxyureide (III; R = CO·NH·CO·NH_2).—3,4-Diaminopyridine (8 g.) in ethanol (200 c.c.) was added to a cold solution of alloxan monohydrate (17 g.) in ethanol (200 c.c.), and the yellow precipitate (16·5 g., 96%) was collected after 4 hr. and washed with water and with methanol. The *ureide* was obtained as a yellow powder, m. p. 238—240° (decomp.) (Found: C, 45·9; H, 3·3; N, 29·8. $C_9H_7N_5O_3$ requires C, 46·4; H, 3·0; N, 30·0%).

1,2,3,4-Tetrahydro-2-oxo-1,4,6-triazanaphthalene-3-spiro-5′-hydantoin (V; R = H).—The foregoing ureide (2 g.) was boiled with acetic acid (10 c.c.) for 30 min. The *spiran* separated from the cold solution; recrystallisation gave needles (1·7 g., 85%), m. p. 257—258° (decomp.) (Found: C, 45·9; H, 3·3; N, 29·8. $C_9H_7N_5O_3$ requires C, 46·4; H, 3·0; N, 30·0%). Similar cyclisation occurred in 2N-hydrochloric acid and in 2N-sodium hydroxide.

1,2,3,4-Tetrahydro-1-methyl-2-oxo-1,4,6-triazanaphthalene-3-spiro-5′-hydantoin (V; R = Me).—Alloxan monohydrate (8·3 g.) in water (100 c.c.) was added to a solution of 3-amino-4-methylaminopyridine (4 g.) in ethanol (75 c.c.), and the product was collected after 6 hr. at room temperature. Recrystallisation from water (charcoal) gave the *spiran* (5·9 g., 73%) in needles, m. p. 225—226° (decomp.) (Found: C, 45·2; H, 4·1; N, 26·5. $C_{10}H_9N_5O_3,H_2O$ requires C, 45·3; H, 4·2; N, 26·4%). The hydantoin dissolved in aqueous alkali to give a colourless solution; in ethanol or acetic acid it showed a blue fluorescence under ultraviolet light.

1,2,3,4-Tetrahydro-1,1′,3′-trimethyl-2-oxo-1,4,6-triazanaphthalene-3-spiro-5′-hydantoin (VI).—(*a*) Ethereal diazomethane (from methylnitrosourea, 30 g.) was added to 1,2,3,4-tetrahydro-1-methyl-2-oxo-1,4,6-triazanaphthalene-3-spiro-5′-hydantoin (2·2 g.) in methanol (250 c.c.). Next day the solvents were removed under reduced pressure, and crystallisation of the residue from ethanol–hexane (charcoal) gave the *trimethyl-spiran monohydrate* in plates (1·2 g., 50%), m. p. 185° (Found: C, 49·2; H, 5·1; N, 23·6; *N*-Me, 12·1. $C_{12}H_{13}N_5O_3,H_2O$ requires C, 49·1; H, 5·2; N, 23·9; *N*-Me, 15·3%).

(*b*) A stirred suspension of 2-hydroxy-1,4,6-triazanaphthalene-3-carboxyureide (1·1 g.) was treated with ethereal diazomethane from methylnitrosourea (20 g.), and the mixture was kept at 0° for 4 hr. before the addition of further ethereal diazomethane (from methylnitrosourea, 30 g.). After 24 hr. at room temperature the solvents were evaporated under reduced pressure and crystallisation from ethanol–hexane (charcoal) gave the trimethyl-spiran in plates, m. p. 185° alone and when mixed with that prepared by method (*a*).

4,1′-Diacetyl-1,2,3,4-tetrahydro-1-methyl-2-oxo-1,4,6-triazanaphthalene-3-spiro-5′-hydantoin.—The spiran (V; R = Me) (0·5 g.) was boiled with acetic anhydride (30 c.c.) and, when a clear solution was obtained (15 min.), acetyl chloride (10 c.c.) was added and the solution was boiled under reflux for 30 min. Evaporation under reduced pressure left a residue of the *diacetyl-spiran* (0·4 g.), which crystallised from aqueous ethanol (charcoal) in prisms (0·23 g., 34%), m. p. 272° (decomp.) after being dried at 175°/1 mm. for 6 hr. (Found: C, 50·2; H, 4·0; N, 20·7. $C_{14}H_{13}N_5O_5$ requires C, 50·8; H, 4·0; N, 21·1%). Solutions in ethanol and in acetic acid showed blue fluorescence in ultraviolet light.

1,2,3,4-Tetrahydro-4-methyl-3-oxo-1,4,6-triazanaphthalene-2-spiro-5′-hydantoin (IX).—4-Amino-3-methylaminopyridine (0·6 g.) in ethanol (15 c.c.) was added to alloxan monohydrate (1·25 g.) in ethanol (25 c.c.) and the product was collected after 6 hr. and washed with water

and with methanol. Recrystallisation from aqueous ethanol (charcoal) gave the *spiran* (IX) (1·1 g., 90%) in needles, m. p. 167° (Found: C, 48·0; H, 3·8; N, 28·1; O, 19·7. $C_{10}H_9N_5O_3$ requires C, 48·6; H, 3·7; N, 28·3; O, 19·4%). The compound dissolved in aqueous sodium hydroxide, and an ethanolic solution showed blue fluorescence under ultraviolet light.

Ethyl 2-*Hydroxy*-1,4,6-*triazanaphthalene*-3-*carboxylate* (III; R = CO_2Et) *and* 3-*Hydroxy*-1,4,6-*triazanaphthalene*-2-*carboxylate* (VII; R = CO_2Et).—Diethyl mesoxalate (12 c.c.) in ethanol (20 c.c.) was added to 3,4-diaminopyridine (5 g.) in ethanol (100 c.c.), and the mixture was heated on a steam-bath for 30 min. Material which crystallised from the cold solution recrystallised from ethanol and gave a mixture (7 g., 70%) which was separated by fractional crystallisation from ethanol into *ethyl* 2-*hydroxy*-1,4,6-*triazanaphthalene*-3-*carboxylate* (6·5 g., 65%), yellow needles, m. p. 227—228° (decomp.) (Found: C, 54·5; H, 4·0; N, 18·8%), and *ethyl* 3-*hydroxy*-1,4,6-*triazanaphthalene*-2-*carboxylate* (0·06 g., 0·6%), yellow prisms, m. p. 153—154° (Found: C, 54·4; H, 4·4; N, 18·7. $C_{10}H_9N_3O_3$ requires C, 54·8; H, 4·1; N, 19·2%). The 2-hydroxy-ester was soluble in water and less soluble in other solvents; an ethanolic solution showed a blue fluorescence under ultraviolet light.

Ethyl 1,2-*Dihydro*-1-*methyl*-2-*oxo*-1,4,6-*triazanaphthalene*-3-*carboxylate* (IV; R = CO_2Et).—3-Amino-4-methylaminopyridine (2 g.) in ethanol (50 c.c.) was added to a solution of diethyl mesoxalate (3·5 g.) in ethanol (10 c.c.), and the mixture was heated on a steam-bath and stirred for 30 min. Recrystallisation of the solid product from ethanol–hexane (charcoal) gave the *ester* (3·12 g., 82%) in needles, m. p. 176° (Found: C, 56·7; H, 4·7; N, 18·0. $C_{11}H_{11}N_3O_3$ requires C, 56·7; H, 4·8; N, 18·0%). The compound dissolved in hot water and in dilute acid, but was sparingly soluble in most solvents. The ester (1·53 g., 50%), m. p. and mixed m. p. 176°, was also obtained by treating ethyl 2-hydroxy-1,4,6-triazanaphthalene-3-carboxylate (3·0 g.) with diazomethane.

Ethyl 3,4-*Dihydro*-4-*methyl*-3-*oxo*-1,4,6-*triazanaphthalene*-2-*carboxylate* (VIII; R = CO_2Et).—Diethyl mesoxalate (1·75 g.) in ethanol (10 c.c.) was added dropwise to a stirred solution of 4-amino-3-methylaminopyridine (1·0 g.) in ethanol (20 c.c.), and the mixture was heated on a steam-bath for 2 hr. The solution was evaporated under reduced pressure and the residue of bicyclic *ester* crystallised from benzene–hexane (charcoal) in needles (1·11 g., 58%), m. p. 127° (Found: C, 56·4; H, 4·7; N, 17·9. $C_{11}H_{11}N_3O_3$ requires C, 56·7; H, 4·8; N, 18·0%). Ethyl 3-hydroxy-1,4,6-triazanaphthalene-2-carboxylate and diazomethane similarly gave the *N*-methyl derivative, m. p. and mixed m. p. 127° (Found: *N*-Me, 9·1; OEt, 18·3. $C_{11}H_{11}N_3O_3$ requires *N*-Me, 12·5; OEt, 19·3%).

2-*Hydroxy*-1,4,6-*triazanaphthalene*-3-*carboxylic Acid* (III; R = CO_2H).—(*a*) Ethyl 2-hydroxy-1,4,6-triazanaphthalene-3-carboxylate (3 g.) was heated with 2N-sodium hydroxide (30 c.c.) on a steam-bath for 2 hr. and the solution was then acidified. Recrystallisation of the solid from aqueous ethanol gave the corresponding acid as *dihydrate* (2·32 g., 75%), m. p. >380° (decomp.) (Found: C, 42·5; H, 4·1; N, 18·8. $C_8H_5N_3O_3,2H_2O$ requires C, 42·3; H, 4·0; N, 18·5%), sparingly soluble in ethanol and in water.

(*b*) 2-Hydroxy-1,4,6-triazanaphthalene-3-carboxyureide (2·0 g.) was heated on a steam-bath with 2N-sodium hydroxide (50 c.c.) for 4 hr. to give the hydrated acid (0·8 g., 40%) (Found: C, 41·8; H, 4·0; N, 18·2%).

(*c*) The acid was also obtained, as colourless needles (1·68 g., 80%), when 3,4-diaminopyridine (1 g.) and diethyl mesoxalate (1·5 c.c.) were heated with N-hydrochloric acid (25 c.c.) on a steam-bath for 2 hr. (Found: C, 42·5; H, 4·0%).

1,2-*Dihydro*-1-*methyl*-2-*oxo*-1,4,6-*triazanaphthalene*-3-*carboxylic Acid* (IV; R = CO_2H).—(*a*) Ethyl 1,2-dihydro-1-methyl-2-oxo-1,4,6-triazanaphthalene-3-carboxylate (1·0 g.) was heated in 2N-hydrochloric acid (30 c.c.) on a steam-bath for 30 min. The cooled solution deposited yellow prisms of the derived *acid* which crystallised from aqueous ethanol (charcoal) in colourless needles (0·56 g., 64%), decomp. 214—215° (Found: N, 20·0. $C_9H_7N_3O_3$ requires N, 20·5%).

(*b*) 1,2,3,4-Tetrahydro-1-methyl-2-oxo-1,4,6-triazanaphthalene-3-spiro-5′-hydantoin (1 g.) was heated on a steam-bath for 2 hr. with 2N-potassium hydroxide (20 c.c.). Acidification gave the acid which crystallised from aqueous ethanol (charcoal) in needles, m. p. and mixed m. p. 213—215° (decomp.).

(*c*) A methanolic solution (100 c.c.) of 2-hydroxy-1,4,6-triazanaphthalene-3-carboxylic acid (0·5 g.) was treated with ethereal diazomethane for 2 hr. The solvent was evaporated and the residue was boiled with 2N-hydrochloric acid, which gave the above 1-methyl-2-oxo-acid (0·11 g., 24%).

1,2-*Dihydro*-1-*methyl*-2-*oxo*-1,4,6-*triazanaphthalene* (IV; R = H).—1,2-Dihydro-1-methyl-2-oxo-1,4,6-triazanaphthalene-3-carboxylic acid (1·0 g.) was heated at 190° under nitrogen for 2—3 min., and sublimation of the residue at 200°/15 mm. then gave 1,2-*dihydro*-1-*methyl*-2-*oxo*-1,4,6-*triazanaphthalene* (0·41 g., 52%) in colourless needles, m. p. 174—176°, raised by recrystallisation from light petroleum (b. p. 60—80°) to m. p. 177° (Found: C, 59·5; H, 4·3. $C_8H_7N_3O$ requires C, 59·6; H, 4·4%).

3,4-*Dihydro*-4-*methyl*-3-*oxo*-1,4,6-*triazanaphthalene*-2-*carboxylic Acid* (VIII; R = CO_2H).—(*a*) 1,2,3,4-Tetrahydro-4-methyl-3-oxo-2-spiro-5′-hydantoin (0·5 g.) was heated with 2N-hydrochloric acid on a steam-bath for 2 hr., and the solution was then continuously extracted with chloroform. The dried extract ($MgSO_4$) was evaporated, and crystallisation of the residue from benzene–hexane (charcoal) gave 3,4-*dihydro*-4-*methyl*-3-*oxo*-1,4,6-*triazanaphthalene*-2-*carboxylic acid* (0·2 g., 48%) in colourless prisms, m. p. 286—288° (decomp.) (Found: C, 52·1; H, 3·7; N, 20·1. $C_9H_7N_3O_3$ requires C, 52·7; H, 3·4; N, 20·5%). The acid became red on exposure to air.

(*b*) Ethyl 3,4-dihydro-4-methyl-3-oxo-1,4,6-triazanaphthalene-2-carboxylate (0·75 g.) was heated in 2N-hydrochloric acid (15 c.c.) on a steam-bath for 2 hr. and the solution was then continuously extracted with chloroform. Evaporation of the dried ($MgSO_4$) extract and crystallisation of the residue from benzene–hexane gave the acid (0·29 g., 44%) in prisms, m. p. and mixed m. p. 286—288° (decomp.). Alkaline hydrolysis of the ester and the derived spirohydantoin similarly gave the acid. The same acid was obtained (60%) directly from 4-amino-3-methylaminopyridine and ethyl mesoxalate by condensation in boiling N-hydrochloric acid.

3,4-*Dihydro*-4-*methyl*-3-*oxo*-1,4,6-*triazanaphthalene* (VIII; R = H).—Pyrolysis of 3,4-dihydro-4-methyl-3-oxo-1,4,6-triazanaphthalene-2-carboxylic acid (0·43 g.) at 180° under nitrogen for 2—3 min., and sublimation of the residue under reduced pressure, gave 3,4-*dihydro*-4-*methyl*-3-*oxo*-1,4,6-*triazanaphthalene* (0·13 g., 36%), m. p. 138—140°. This crystallised from light petroleum (b. p. 60—80°) in colourless needles, m. p. 145°, and became coloured when exposed to air (Found: C, 59·8; H, 4·4; N, 25·9. $C_8H_7N_3O$ requires C, 59·6; H, 4·4; N, 26·1%).

2-*Hydroxy*-1,4,6-*triazanaphthalene*-3-*carboxyamide* (III; R = $CO{\cdot}NH_2$).—Ethyl 2-hydroxy-1,4,6-triazanaphthalene-3-carboxylate (0·3 g.) was heated on a steam-bath with aqueous ammonia (*d* 0·88; 6 c.c.) for 30 min. The amide was collected, and recrystallisation from aqueous ethanol gave the *amide* (0·26 g., 99%) in yellow plates, decomp. >315° (Found: C, 50·5; H, 3·3; N, 29·2. $C_8H_6N_4O_2$ requires C, 50·5; H, 3·2; N, 29·5%). An ethanolic solution showed blue fluorescence under ultraviolet light.

3-*Hydroxy*-1,4,6-*triazanaphthalene*-2-*carboxyamide* (VII; R = $CO{\cdot}NH_2$).—Ethyl 3-hydroxy-1,4,6-triazanaphthalene-2-carboxylate (0·1 g.) was converted, similarly to the isomer described above, into the *amide* (0·08 g., 92%) which crystallised from aqueous ethanol in yellow prisms, m. p. 355° (decomp.) (Found: C, 48·4; H, 3·5; N, 27·8. $C_8H_6N_4O_2,\frac{1}{2}H_2O$ requires C, 48·2; H, 3·5; N, 28·1%).

1,2-*Dihydro*-1-*methyl*-2-*oxo*-1,4,6-*triazanaphthalene*-3-*carboxyamide* (IV; R = $CO{\cdot}NH_2$).—Ammonolysis of the corresponding ester (2 g.) with aqueous ammonia (*d* 0·88, 35 c.c.) on a steam-bath for 30 min. gave the *amide*, needles (from ethanol; charcoal) (1·69 g., 96%), m. p. 253—254° (decomp.) (Found: C, 53·0; H, 4·0; N, 27·0. $C_9H_8N_4O_2$ requires C, 52·9; H, 4·0; N, 27·4%).

3,4-*Dihydro*-4-*methyl*-3-*oxo*-1,4,6-*triazanaphthalene*-2-*carboxyamide* (VIII; R = $CO{\cdot}NH_2$).—Saturated ethanolic ammonia (20 c.c.) was added to a solution of 3,4-dihydro-4-methyl-3-oxo-1,4,6-triazanaphthalene-3-carboxylate (0·5 g.) in ethanol (10 c.c.), and the mixture was heated on a steam-bath for 30 min. Recrystallisation of the solid product from ethanol gave the *amide* in needles, m. p. 262—263° (decomp.) (Found: C, 53·0; H, 4·0; N, 26·7. $C_9H_8N_4O_2$ requires C, 52·9; H, 4·0; N, 27·4%).

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