Tautomerism of *N*-Heterocycles. Part II.[1] 3-Hydroxypyridazin-6-one and 3-Mercaptopyridazine-6-thione

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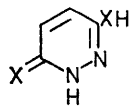
Ionization constants and u.v. spectra of 3,6-dimercaptopyridazine and its *N*- and *S*-methyl derivatives reveal that the parent compound exists in aqueous solution as 3-mercaptopyridazine-6-thione.

3,6-Dihydroxypyridazine, its *NN*'-dimethyl derivative, and 3-hydroxypyridazine on protonation behave abnormally.

TAUTOMERISM in 3,6-dihydroxypyridazine †, [2-10] and 3,6-dimercaptopyridazine [6a,11,12] has previously been investigated extensively by several techniques in the solid state and in a variety of solvents. For aqueous solutions however, published data were incomplete, and some appeared to require further investigation.[11,13]

Ionization constants and u.v. spectra of the various species of pure 3,6-dihydroxy- and 3,6-dimercaptopyridazine and of all possible *N*-, *O*-, and *S*-dimethyl derivatives are recorded in the Table together with those for 3-hydroxypyridazine and the relevant literature data. The u.v. spectra of the neutral species (and pK_a values) confirm that 3,6-dihydroxypyridazine, as established earlier,[8a] exists in aqueous solution predominantly in the form (1; X = O). The spectra of the neutral species of 3,6-dimercaptopyridazine show that this too exists predominantly in the form (1) (X = S); the spectral data are similar to those of 1-methyl-3-methylthiopyridazine-6-thione and 6-mercapto-3-methylthiopyridazine but differ from those of 3,6-bismethylthiopyridazine and 1,2-dimethylpyridazine-3,6-dithione.



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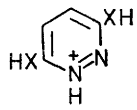

(2)

With respect to the cations, the u.v. spectrum of 3,6-dihydroxypyridazine resembled those of 3,6-dimethoxypyridazine and 3-methoxy-1-methylpyridazin-6-one but differed significantly from that of 1,2-dimethylpyridazine-3,6-dione, clearly indicating that the cation of 3,6-dihydroxypyridazine had the structure (2; X = O). The spectra for the monocations of 3,6-dimercaptopyridazine (basic pK_a −2·55), its dimethyl derivatives, and 3,6-bismethylthiopyridazine methiodide showed that the dimercapto-compound too had the structure (2) (X = S).

Redetermination of the basic pK_a of 3,6-dihydroxypyridazine gave an unusual result. As in the initial determination,[13] the data at different H_0 values did not give a constant pK_a value, but a value which fell with increasing acidity. Refinement of the technique [14] revealed that the data could be explained by the existence of two overlapping ionization constants. 1,2-Dimethylpyridazine-3,6-dione behaved similarly; and re-examination of 3-hydroxypyridazine showed a similar phenomenon, not shared by 4-hydroxypyridazine (*cf.* ref. 15). In the case of the 3-hydroxy-compounds, a possible explanation is that the position of tautomeric equilibrium is shifted in solutions of greater acidity, so that two equilibria exist simultaneously, as has now been suggested for 3,6-dihydroxypyridazine.[16] However the u.v. spectra of the cations of 3-hydroxy- and 3,6-dihydroxy-pyridazine and their methylated derivatives do not support this contention, unless the shift in equilibrium occurs only to a minor degree.

The possibility that this unusual behaviour is due to decomposition cannot be completely excluded. Solutions of 3-hydroxy- and 3,6-dihydroxy-pyridazine and of 1,2-dimethylpyridazine-3,6-dione in acid sufficiently concentrated to give the cation (see Table) were neutralized after 5 min, and the u.v. spectra of the neutral species were examined. Those of the products from 3-hydroxypyridazine and 1,2-dimethylpyridazine-3,6-dione did not differ significantly from those of untreated specimens, but the product from 3,6-dihydroxypyridazine did show an increase of 10% in the ε value at 301 nm.

No ^{1}H n.m.r. evidence was found for hydration in these compounds.

The ionization constants of 3,6-dimercaptopyridazine and its methyl derivatives did not reveal any of the

† Throughout this paper terms such as hydroxy and mercapto will be used for convenience without any implication as to the predominant tautomeric form.

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abnormal behaviour observed with their oxygen analogues. The similarity of the pK_a values of 3,6-dimercaptopyridazine to those of 1-methyl-3-methylthiopyridazine-6-thione and 6-mercapto-3-methylthiopyridazine established the existence of the parent compound azine the pK_a of 1·95 was of the magnitude expected (*cf.* the value of −6·0 advanced by Stanovnik and Tišler [11]).

For this work 3,6-dimercaptopyridazine [17] was purified through 3,6-bisbenzoylthiopyridazine, to remove any

Physical properties (pK_a values and spectra)

	Ionization (water; 20°)					Spectroscopy in water [c]		
Pyridazine	Charged species involved [a]	pK_a	Spread (±)	Concn. (M)	A.w.l.[b] (nm)	$\lambda_{max.}$/nm	log ε	pH [d]
3-OH	0					220, 281 [e]	3·50, 3·45	6·0
	+	−1·27 [f,g]	0·07	0·00006	285			
		−2·42 [g,h]	0·06	0·00006	285	215, 265 [i,j]	3·44, 3·41	−3·6
N(1)-Me-3-O⁻	0					309 [k]	3·71	5·0
	+	2·31 [k]				274 [k]	3·78	0·0
N(2)-Me-3-(=O)	0					225, 287 [l]	3·38, 3·51	4·35
	+	−2·1 [l]				*210*, 265 [l]	*3·44*, 3·49	−5·0
3-OMe	0					<210, 265 [i]	>3·48, 3·37	6·0
	+	2·52 [m]				217, 369 [i]	3·40, 3·30	0·0
3,6-$(OH)_2$	0					204, *226*, 301 [n,o]	4·18, *3·66*, 3·39	2·0
	+	−0·99 [p,q]	0·11	0·0001	310			
		−3·28 [q,r]	0·10	0·0001	310	*216*, 283 [s]	*3·66*, 3·45	−5·0
	−	5·67 [m]				217, *235*, 328 [o]	4·17, *3·91*, 3·37	8·0
	−−	13 [m]				*238*, 333	*3·88*, 3·43	15·0
1,2-Me_2-3,6-(=O)$_2$	0					213, *236*, 324 [n,o]	4·15, *3·53*, 3·43	5·0
	+	−1·94 [t]	0·08	0·0001	280			
		−3·96 [u]	0·16	0·0001	280	206, *232*, 297 [v]	4·26, *3·42*, 3·54	−6·3
1-Me-3-OMe-6-(=O)	0					(209), *223*, 300, 304 [n,o]	(4·18), *3·81*, 3·42, 3·42	5·0
	+	−0·91	0·05	0·0005	320	(202), *222*, 288	(4·26), *3·64*, 3·42	−3·0
3,6-$(OMe)_2$	0					283·5 [w]	3·31	4·0
	+	1·61 [m]				284	3·35	−0·5
3,6-$(SH)_2$	0					(223), 293, 363 [x]	(3·64), 4·27, 3·48	0·0
	+	−2·55 [y]	0·04	0·00001	305	269, *336* [x]	4·23, *3·33*	−4·4
	−	2·06 [y]	0·04	0·00001	315	(*223*,) 307, *372* [x]	(*3·85*), 4·46, *3·27*	7·0
	−−	10·36 [y]	0·04	0·00001	315	*230*, 283, *350* [x]	*3·91*, 4·38, *3·18*	13·0
1,2-Me_2-3,6-(=S)$_2$	0					215, 310, *348*	3·89, 4·46, *3·82*	5·0
	+	−4·10	0·06	0·00002	320	293	4·35	−5·7
1-Me-3-SMe-6-(=S)	0					227, 290, 364	3·40, 4·41, 3·39	5·0
	+	−2·55	0·05	0·00001	300	276, 338	4·37, 3·14	−4·4
3-SH-6-SMe	0					293, 368	4·36, 3·42	5·0
	+	−2·62	0·05	0·000015	310	278, *330*	4·30, *3·37*	−4·4
	−	8·19	0·05	0·0001	310	223, 286, *365*	3·73, 4·31, *3·01*	11·0
3,6-$(SMe)_2$	0					*222*, 271, *320*	*3·42*, 4·28, *3·10*	5·0
	+	1·95 [z]	0·04	0·000015	285	283, 342 [x]	4·34, 3·22	−0·3
3,6-$(SMe)_2$,MeI	+					282, 348	4·43, 3·28	7·0
1,2-Me_2-3-(=O)-6-(=S)	0					213, 261, 367	3·82, 4·22, 3·68	5·0
	+	<−3·0 [aa]						

[a] 0, neutral species; +, cation; −, anion; −−, dianion. [b] Analytical wavelength for spectrosopic determinations of pK_a. [c] Shoulders and inflections in italics. [d] pH Values below 0 obtained in solutions of hydrochloric or sulphuric acid to which Hammett acidity functions (*cf.* M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1) have been assigned. For H⁻ functions see G. Yagil and M. Anbar, *J. Amer. Chem. Soc.*, 1963, **85**, 2376. [e] S. F. Mason, *J. Chem. Soc.*, 1957, 5010. [f] Computed from density readings for nine solutions in the range H_0 0·0 to −1·8. [g] Ref. 17 gives pK_a −1·40 ± 0·1; ref. 13 gives −1·8 ± 0·3. [h] Computed from density readings for eight solutions in the range H_0 −2·0 to −3·4. [i] S. F. Mason, *J. Chem. Soc.*, 1959, 1253. [j] A solution of 3-hydroxypyridazine in 8·3M-sulphuric acid set aside for 6 min and then neutralized to pH 4 gave the u.v. spectrum ($\lambda_{max.}$ and ε) of the neutral species. [k] Ref. 1. [l] A. Albert and G. B. Barlin, *J. Chem. Soc.*, 1962, 3129. [m] Ref. 13. [n] Ref. 9*b* gives the u.v. spectrum in 95% ethanol; ref. 6*a* gives the u.v. spectrum in alcohol. [o] Ref. 8*a* gives the spectral curves in aqueous 0·1N-hydrochloric acid and pH 8·40 buffer solutions. [p] Computed from density readings for ten solutions in the range H_0 −0·2 to −2·0. [q] Ref. 13 gives pK_a −2·2 ± 0·4; ref. 17 gives −0·97 ± 0·01. [r] Computed from density readings for eight solutions in the range H_0 −2·4 to −3·8. [s] A sample in 9·3M-sulphuric acid kept at 20° for 5 min on neutralization with aqueous potassium hydroxide to pH 2·0 gave the same $\lambda_{max.}$ as the spectrum of the neutral species but with an increase of 10% in the ε value. [t] Computed from density readings for eight solutions in the range H_0 −1·2 to −2·6; a check at 350 nm gave pK_a −2·10 ± 0·14. [u] Computed from density readings for eight solutions in the range H_0 −3·2 to −4·6; a check at 350 nm gave pK_a −4·06 ± 0·11. [v] A sample in 12M-sulphuric acid kept at 20° for 5 min on neutralization with aqueous potassium hydroxide gave the same $\lambda_{max.}$ and ε values as the neutral species. [w] S. F. Mason, *J. Chem. Soc.*, 1959, 1247 gives $\lambda_{max.}$ 284 nm and log ε 3·36 at pH 7·0. [x] Ref. 11 gives some spectral peaks at many pH (H_0) values. [y] Ref. 11 gives pK_a values −3·0, −0·5, 2·1, and 10·4. [z] Ref. 11 gives pK_a −6·0. [aa] Apparent instability. Isosbestic points not given by solutions of $H_0 < -3$.

in the form (1; X = S). The three pK_a values of 3,6-dimercaptopyridazine (−2·55, 2·06, 10·36) were of similar magnitude to those reported by Stanovnik and Tišler,[11] but no evidence could be found for the pK_a of −0·5 claimed by these authors. For 3,6-bismethylthiopyridpartially thiated compound or disulphide, and the free dimercapto-compound was liberated by acidic hydrolysis.

Heating 3,6-bismethylthiopyridazine methiodide in

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t-butyl alcohol on a steam-bath gave 1-methyl-3-methylthiopyridazine-6-thione. 3,6-Bismethylthiopyridazine ethiodide under similar conditions gave 1-ethyl-3-methylthiopyridazine-6-thione.

EXPERIMENTAL

Analyses were performed by the Australian National University Analytical Services Unit. Solids for analysis were dried at 100° unless otherwise stated, and m.p.s were taken for samples in Pyrex capillaries. All compounds were recrystallized to constant m.p. unless otherwise stated and were further examined for the presence of impurities by paper chromatography on Whatman No. 1 paper with (*a*) aqueous 3% ammonium chloride, or (*b*) butan-2-ol–5N-acetic acid (7 : 3) as solvent, and by t.l.c.

Ionization constants were determined spectroscopically [18] by Mr. I. Hawkins. U.v. spectra were measured with a Perkin-Elmer 450 recording spectrophotometer and $\lambda_{max.}$ and ε values were checked with an Optical CF4 manual instrument (Mr. D. Light).

3,6-Dihydroxypyridazine,[19] m.p. 310—312° (lit.,[19] 299·5—300°) (Found: C, 42·9; H, 3·6; N, 25·0. Calc. for $C_4H_4N_2O_2$: C, 42·9; H, 3·6; N, 25·0%), was converted *via* the dichloro-[19] into the dimethoxy-compound,[20] m.p. 104° (lit.,[20] 108°). 1,2-Dimethylpyridazine-3,6-dione, obtained from 1,2-dimethylhydrazine dihydrochloride and maleic anhydride [9a] and also by methylation [21] of 3,6-dihydroxypyridazine, had m.p. 140—142° (lit.,[9a] 137—138°). 3-Methoxy-1-methylpyridazin-6-one, from 3,6-dihydroxypyridazine and dimethyl sulphate,[9a] had m.p. 63—65° (lit.,[9a] 64—65°).

3,6-*Bisbenzoylthiopyridazine*.—3,6-Dimercaptopyridazine [from 3,6-dichloropyridazine (5·0 g) and thiourea (5·4 g) [17]] was dissolved in 5N-sodium hydroxide (30 ml), benzoyl chloride (10·0 ml) was added, and the mixture was shaken. The solid (5·1 g) was filtered off, washed, dried, and recrystallized from benzene to give white crystals of 3,6-*bisbenzoylthiopyridazine*, m.p. 196° (Found: C, 61·5; H, 3·5; N, 8·0; S, 18·1. $C_{18}H_{12}N_2O_2S_2$ requires C, 61·4; H, 3·4; N, 7·95; S, 18·2%). Recrystallization of the crude product from ethanol gave yellow crystals of 3-*benzoylthio*-6-*mercaptopyridazine* (2·25 g), m.p. 214—215° (Found: C, 53·5; H, 3·6; N, 11·2; S, 25·9. $C_{11}H_8N_2OS_2$ requires C, 53·2; H, 3·25; N, 11·3; S, 25·8%).

3-Benzoylthio-6-mercaptopyridazine (0·1 g), N-sodium hydroxide (5·0 ml), and benzoyl chloride (0·2 ml) were shaken for *ca.* 30 min. The solid (0·103 g) was collected, dried, and recrystallized from benzene to give 3,6-bisbenzoylthiopyridazine, m.p. and mixed m.p. 194°.

3,6-*Dimercaptopyridazine*.— 3,6-Bisbenzoylthiopyridazine (0·8 g) and 5N-hydrochloric acid (40 ml) were refluxed for 2 h. After cooling, the precipitate was collected, dried, washed with benzene, dissolved in N-sodium hydroxide, and reprecipitated by addition of 2N-hydrochloric acid to pH 0·5 to give 3,6-dimercaptopyridazine (0·255 g), m.p. 260—262° (decomp.) [lit.,[20] 230—240° (decomp.); lit.,[22] 255° (decomp.)] (Found: C, 33·5; H, 2·6; N, 19·2; S, 44·4. Calc. for $C_4H_4N_2S_2$: C, 33·3; H, 2·8; N, 19·4; S, 44·5%).

Similar hydrolysis of 3-benzoylthio-6-mercaptopyridazine also gave 3,6-dimercaptopyridazine.

Reaction of 1,2-*Dimethylpyridazine*-3,6-*dione with Phosphorus Pentasulphide in Benzene*.—A mixture of 1,2-dimethylpyridazine-3,6-dione (0·5 g), phosphorus pentasulphide (2·5 g), and benzene (50 ml) was refluxed for 7·5 h. The solvent was evaporated off under reduced pressure and water was added. The mixture was warmed to decompose the excess of reagent, adjusted to pH *ca.* 5, and extracted with chloroform to give a yellow solid. This solid was extracted with a little cold acetone and gave a soluble and an insoluble fraction.

The acetone-insoluble product was dissolved in chloroform and chromatographed over alumina (21 in). The product from the first yellow band was extracted with cyclohexane and the insoluble material was recrystallized from ethanol to give 1,2-*dimethylpyridazine*-3,6-*dithione* (0·050 g), m.p. 209—210° (Found: C, 42·2; H, 4·8; N, 15·95; S, 37·2. $C_6H_8N_2S_2$ requires C, 41·8; H, 4·7; N, 16·3; S, 37·2%).

The acetone-soluble product was dissolved in ethyl acetate and chromatographed over alumina (12 in). The second yellow band afforded 1,2-*dihydro*-1,2-*dimethyl*-6-*thioxopyridazin*-3-*one* (0·051 g), m.p. 143—145° (from ethanol) (Found: C, 46·5; H, 5·4; N, 17·5; S, 20·55. $C_6H_8N_2OS$ requires C, 46·1; H, 5·2; N, 17·9; S, 20·5%).

Methylation of 3,6-*Dimercaptopyridazine*.—Treatment of 3,6-dimercaptopyridazine [17,23] (3 g) with methyl iodide (3 g) in methanolic potassium hydroxide [12] gave 3,6-bismethylthiopyridazine, m.p. 130—131° (lit.,[20] 128—129°), and 3-mercapto-6-methylthiopyridazine, m.p. 150—152° (lit.,[12] 148—149°) (Found: C, 38·1; H, 3·4; N, 18·1; S, 40·0. Calc. for $C_5H_6N_2S_2$: C, 38·0; H, 3·8; N, 17·7; S, 40·5%).

Treatment of 3,6-dimercaptopyridazine (1·5 g) with dimethyl sulphate (2·5 g) in aqueous methanolic sodium hydroxide [12] gave, after t.l.c. (alumina–benzene and silica–benzene), 3,6-bismethylthiopyridazine and 1-methyl-3-methylthiopyridazine-6-thione, m.p. 86—87° (lit.,[12] 73—74°) (Found, for material dried at 65° for 2 h: C, 42·05; H, 4·55; N, 16·5; S, 37·0. Calc. for $C_6H_8N_2S_2$: C, 41·8; H, 4·7; N, 16·3; S, 37·2%). 3,6-Dimethylthiopyridazine did not rearrange when heated at 150° for 2 h.

3,6-*Bismethylthiopyridazine Methiodide*.—A mixture of 3,6-bismethylthiopyridazine (0·10 g), methanol (1·5 ml), and methyl iodide (1·5 ml) was kept at 20° for 6 days, then evaporated to dryness. The product crystallized from methanol–t-butyl alcohol to give 3,6-*bismethylthiopyridazine methiodide* (0·112 g), m.p. 161—163° (Found: C, 27·1; H, 3·6; N, 8·6. $C_7H_{11}IN_2S_2$ requires C, 26·8; H, 3·5; N, 8·9%).

In another preparation 3,6-bismethylthiopyridazine (0·040 g), t-butyl alcohol (1·0 ml), and methyl iodide (0·5 ml) were kept at 20° for 4 days. The yellow solid (0·030 g) was filtered off, washed with t-butyl alcohol, and dried at 100°. It had m.p. 163—165° (Found: C, 26·8; H, 3·6; N, 8·9%).

1-*Methyl*-3-*methylthiopyridazine*-6-*thione*.— 3,6-Bismethylthiopyridazine methiodide (0·135 g) and t-butyl alcohol (15 ml) were refluxed on a steam-bath for 4 h. The mixture was evaporated to dryness and the product crystallized from light petroleum (b.p. 60—80°) to give 1-methyl-3-methylthiopyridazine-6-thione (0·012 g), m.p. and mixed m.p. 87—88°.

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3,6-*Bismethylthiopyridazine Ethiodide*.—3,6-Bismethylthiopyridazine (0·2 g), ethyl iodide (3 ml), and ethanol (3 ml) were heated in a sealed tube in a steam-bath for 2 h. The mixture was evaporated to dryness and the product crystallized from t-butyl alcohol to give 3,6-*bismethylthiopyridazine ethiodide* (0·309 g), m.p. 136° (Found: C, 30·0; H, 4·2. $C_8H_{13}IN_2S_2$ requires C, 29·3; H, 4·0%).

1-*Ethyl*-3-*methylthiopyridazine*-6-*thione*.— 3,6-Bismethylthiopyridazine ethiodide (0·13 g) and t-butyl alcohol (10 ml) were refluxed on a steam-bath for 18 h. The mixture was then evaporated to dryness and the residue extracted with light petroleum (b.p. 60—80°). The product extracted was subjected to t.l.c. (alumina–chloroform) and recrystallized from light petroleum (b.p. 60—80°) to give yellow crystals of 1-*ethyl*-3-*methylthiopyridazine*-6-*thione* (0·037 g), m.p. 45—46° (Found, for material dried at 20° and 20 mmHg: C, 44·9; H, 5·6; N, 15·1. $C_7H_{10}N_2S_2$ requires C, 45·1; H, 5·4; N, 15·0%).

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