4′ : 5′-*Dihydroglyoxalino*(2′ : 1′-2 : 3)*thiazolium Salts, and the Ultraviolet Light Absorption of Thiazole Derivatives.*

By WALTER WILSON and R. WOODGER.

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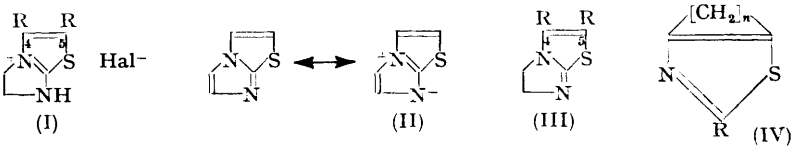
Tetrahydro-2-thioglyoxaline with α-halogenated carbonyl compounds readily affords 4′ : 5′-dihydroglyoxalino(2′ : 1′-2 : 3)thiazolium salts, which are converted by alkali into bicyclic bases of the 2-iminothiazoline type. The ultraviolet light absorption properties of a number of thiazole derivatives are described. 2-Aminothiazoles and 2-iminothiazolines absorb similarly; the higher dipole moments of the latter indicate mesoionic forms. Certain irregularities in the absorption of highly substituted thiazoles are attributed to steric interactions.

EARLIER studies (Wilson, *J.*, 1955, 1389) of the reaction of tetrahydro-2-thioglyoxaline with alkyl halides and alkylene dihalides have now been extended to its reaction with α-halogenated carbonyl compounds. The products (Table 3, p. 2945) are formulated as 4′ : 5′-dihydroglyoxalino(2′ : 1′-2 : 3)thiazolium salts (I) on the basis of their ultraviolet light absorption properties (discussed below) and by analogy with the formation of monocyclic thiazoles from thiourea and α-halogenated carbonyl compounds. The salts (I) contain the same skeleton as " 4 : 5-dihydroglyoxalino-2-thioglycollo-1-lactam " (Stephen and F. J. Wilson, *J.*, 1926, 2532); several derivatives of the aromatic parent system (II) have also been described (Ochiai, *Ber.*, 1936, **69**, 1650; Andersag and Westphal, *ibid.*, 1937, **70**, 2035; Kondo and Nagasawa, *J. Pharm. Soc. Japan*, 1937, **57**, 1050; Matsukawa and Ban, *ibid.*, 1951, **71**, 756). Alkali converted the salts (I) into the bicyclic bases (III) (Table 3B); the structures of these bases and of other 2-iminothiazolines are discussed below.



There is little published information on the ultraviolet absorption of thiazoles. Ruehle (*J. Amer. Chem. Soc.*, 1935, **57**, 1887) studied a few simple thiazoles; however, the band at 225 mμ (ε 13,000) reported for 4-methylthiazole ethiodide is probably iodide ion absorption (cf. Head and Standing, *J.*, 1952, 1457). Thiazole itself has $\lambda_{max.}$ 240 mμ (ε 4000) (Braude, *Ann. Reports*, 1945, **42**, 128). The few 2-amino- and dihydro-2-imino-thiazoles which have been compared appear to have similar spectra (Vandenbelt and Doub, *J. Amer. Chem. Soc.*, 1944, **66**, 1633; Shepherd, Bratton, and Blanchard, *ibid.*, 1942, **64**, 2532). However, there appear to be differences between the absorption of 2-amino- and dihydro-2-imino-benzothiazoles (Edisbury, Hunter, and Scott, *J.*, 1948, 1497), and in view of the successful application of ultraviolet absorption studies to tautomeric 2-aminopyridine systems (Anderson and Seeger, *J. Amer. Chem. Soc.*, 1949, **71**, 340; Gol'dfarb, Setkina, and Danyushevskii, *J. Gen. Chem. U.S.S.R.*, 1948, **18**, 124) further work on 2-iminothiazolines was desirable. The ultraviolet absorption properties of several thiazoles, more complex

than those discussed here, have been reported (Cook, Heilbron, *et al.*, *J.*, 1947, 1598; 1948, 201, 2031; Stern, *J.*, 1949, **1664**; Yamamoto, *J. Pharm. Soc. Japan*, 1951, **71**, 662).

The ultraviolet absorption characteristics of a number of thiazole derivatives, in each case as the base and as the salt, have been measured (Table 1). The introduction of a methyl group at position 4 or 5 or into a 2-amino-group of simple thiazoles has a small bathochromic effect (2—6 mμ), which is seen in both bases and salts. A 4-benzyl group has a similar effect. Methylation of more highly substituted thiazoles sometimes results in a hypsochromic shift, presumably because of steric interaction between the methyl and adjacent groups (see below). Classical tautomerism is impossible in the 2-diethylamino-thiazole (18) and in the 2-iminothiazolines (31) and (25); these three compounds have comparable light absorption either as base or as salt. These results confirm the view

TABLE 1. *Ultraviolet light absorption, in ethanol, of thiazoles and 2-iminothiazolines.*

					Salt		Base	
No.	$R_{(2)}$	$R_{(3)}$	$R_{(4)}$	$R_{(5)}$	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε
1	Dihydroglyoxalino		H	H	264	7,100	270	7,400
2	,,		Me	H	268	6,700	270	8,000
3	,,		Ph·CH_2	H	267	7,400	268	8,700
							234	23,300
4	,,		Ph	H	269	13,200	264	8,400
							310	4,700
5	,,		Ph	Me	272	10,600	234	27,000
							293	7,500
6	,,		Me	Ph	288	12,800	282	8,100
							325	9,800
7	,,		Ph·CH_2	Ph	286	12,600	280	7,300
							324	9,200
8	NH_2	—	Me	H	260	7,300	259	6,400
9	NH_2	—	Ph·CH_2	H	259	7,600	257	5,800
10	NH_2	—	Ph	H	265	16,650	228	23,000
							284	8,000
11	NH_2	—	Ph	Me	265	12,000	256	9,100
12	NH_2	—	H	Ph	290	16,200	308	16,500
13	NH_2	—	Me	Ph	280	13,100	293	11,200
14	NH_2	—	Ph·CH_2	Ph	278	13,200	295	11,500
15	NHMe	—	H	H	258	8,700	261	7,300
16	NHMe	—	Me	H	263	8,700	262	7,300
17	NHMe	—	Ph	H	269	17,500	232	21,400
							288	5,700
18	NEt_2	—	Me	H	224	2,900	269	8,400
					269	9,600		
19	NH_2	—	H	H	255	8,000	255	6,300
20	H	—	Ph	H	252	13,900	252	13,900
21	H	—	Ph	Me	244	11,100	249	11,700
22	H	—	H	Ph	275	12,800	275	12,800
23	H	—	Me	Ph	275	8,500	267	10,700
24	H	—	Me	H	248	3,600	244	3,300
25	:NMe	Me	H	H	255	7,100	259	6,300
26	:NMe	Me	Me	H	260	7,600	257	8,200
27	:NMe	Me	Ph	H	260	12,300	250	9,600
							300	3,900
28	:NMe	Me	Ph	Me	263	11,100	258	9,800
29	:NPh	Ph	Ph	Me	283	9,500	292	11,200
30	:NPh	Ph	Me	Ph	294	12,900	317	13,800
31	:NH	Me	H	H	254	6,800	260	6,400
32	:NH	Me	Me	H	259	6,500	264	6,900
33	:NH	Me	Ph	H	258	10,900	255	8,400
							300	3,900

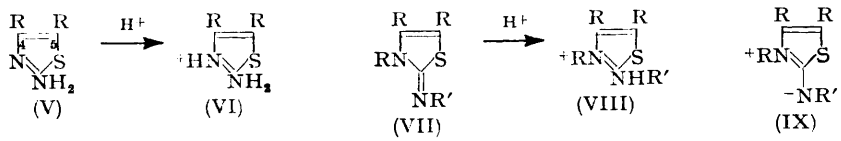
Notes: [8] Salt, $\lambda_{max.}$ 259 mμ (ε 5800) in 95% EtOH (Conover and Tarbell, *J. Amer. Chem. Soc.*, 1950, **72**, 5221). [24] Hydrochloride, $\lambda_{max.}$ 250 mμ (ε 4000), in H_2O (Ruehle, *loc. cit.*). [31] Base, $\lambda_{max.}$ 258 mμ (ε 8000) in EtOH (Shepherd, Bratton, and Blanchard, *loc. cit.*). [19] Base, $\lambda_{max.}$ 254 mμ (ε 6000); hydrochloride, $\lambda_{max.}$ 254 mμ (ε 8000) in H_2O (Vandenbelt and Doub, *loc. cit.*).

(Vandenbelt and Doub, *loc. cit.*) that ultraviolet absorption studies cannot diagnose the tautomeric state of 2-aminothiazoles. It has been established recently by infrared studies that 2-aminothiazole exists as such, and not as 2-iminothiazoline (Angyal and Werner, *J.*, 1952, 2911; cf. Angyal and Angyal, *J.*, 1952, 1461).

Dihydroglyoxalinothiazolium salts and 3-methyl-2-methylaminothiazolium salts are similar in structure; however, the bicyclic compounds absorb at 8—9 mμ longer wavelengths than equivalently substituted monocyclic ones; there is an even greater difference (11—13 mμ) between some of the bases in these two series. The dihydroglyoxaline ring thus has a marked bathochromic effect, which may be associated with ring strain; in that connection, bicyclic thiazoles (IV; $n = 3$) which also have an additional non-aromatic five-membered ring, absorb much less intensely than homologues (IV; $n = 4$) (Erlenmeyer and Schoenauer, *Helv. Chim. Acta*, 1941, **24**, 172E; Erlenmeyer and Bischoff, *ibid.*, 1946, **29**, 280). Steric distortion of chromophoric systems usually results in hypsochromic shifts and/or reduction in intensity (*e.g.*, Braude, Sondheimer, and Forbes, *Nature*, 1954, **173**, 117), although apparent bathochromic shifts have been observed in a few special cases (Meek, Turnbull, and Wilson, *J.*, 1953, 2894).

TABLE 2. *Dipole moments of bases in benzene.*

No.	8	16	10	17	32	26	2	4
Moment (D)	1·8	1·6	2·1	2·3	3·3	3·3	4·2	4·2



The superficial similarity between the absorption curves of 4- or 5-phenylthiazole and 4-methylthiazole is probably not significant; the much more intense absorption of the phenyl compounds is probably a "*K*" band, whilst the non-phenylated compounds exhibit "*B*" bands (cf. Gillam and Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Arnold, London, 1954, p. 125). 2-Amino-5-phenylthiazole hydrochloride (12) absorbs at considerably longer wavelengths than the 4-phenyl

TABLE 3. 4′ : 5′-*Dihydroglyoxalino*(2′ : 1′-2 : 3)*thiazolium salts* (I).

No.	$R_{(4)}$	$R_{(5)}$	Halide used	Yield (%)	M. p.	Formula	Found (%) C	Found (%) H	Calc. (%) C	Calc. (%) H
1	H	H	A	70	183—186°	Hygroscopic, not analysed				
2	Me	H	B	94	258—259	$C_6H_9N_2SCl$	40·95	5·15	40·8	5·15
3	Ph·CH_2	H	G	72	181—183	$C_{12}H_{13}N_2SBr$	48·95	4·35	48·5	4·4
4	Ph	H	C	40	243—244	$C_{11}H_{11}N_2SBr$	46·95	4·0	46·65	3·9
5	Ph	Me	D	80	236—239	$C_{12}H_{13}N_2SBr$	47·6	4·55	48·5	4·4
6	Me	Ph	F	61	246—248	$C_{12}H_{13}N_2SBr$	48·45	4·65	48·5	4·4
7	Ph·CH_2	Ph	H	90	193—194	$C_{18}H_{17}N_2SBr$	57·7	4·45	57·9	4·6

TABLE 3B. *Bicyclic bases* (III) *from dihydroglyoxalinothiazolium salts.*

From salt no.	M. p.	Formula	Found (%) C	Found (%) H	Calc. (%) C	Calc. (%) H
1	84—86°	$C_5H_6N_2S$	47·9	4·8	47·6	4·8
2	90—92	$C_6H_8N_2S,\frac{1}{2}H_2O$	48·6	5·85	48·3	6·1
3	Oil	Unstable, not analysed				
4	111—113	$C_{11}H_{10}N_2S$	65·3	5·05	65·3	5·0
5	90·5—91·5	$C_{12}H_{12}N_2S$	66·4	5·65	66·6	5·6
6	121—124	$C_{12}H_{12}N_2S$	66·2	6·1	66·6	5·6
7	102—103	$C_{18}H_{16}N_2S$	74·5	5·55	73·95	5·5

isomer (10); a similar effect has been observed with the analogous 4- and 5-ethoxycarbonyl compounds (Conover and Tarbell, *J. Amer. Chem. Soc.*, 1950, **72**, 5221). The absorption curves of 2-amino-4-phenylthiazole bases are usually complex, having a main peak, together with a very broad, intense band, within which a second peak can be defined only approximately. 5-Methyl-4-phenylthiazole (21) has anomalous light absorption properties; the hydrochloride absorbs at lower wavelengths (2 mμ) and much less intensely than 4-phenylthiazole hydrochloride (19), and similar effects are seen when the bases are compared. These results are attributed to steric interaction between the methyl and the phenyl group, as

in *o*-substituted diphenyls (*e.g.*, Friedel and Orchin, " Ultra-violet Spectra of Aromatic Compounds," Wiley, New York, 1951). Other examples of this phenomenon can be drawn from Table 1, whilst Knott (*J.*, 1952, 4099) has adduced evidence for steric interaction between 4-phenyl groups and adjacent substituents in more complex thiazole derivatives.

It has been noted already that equivalently substituted 2-aminothiazoles (V) and 2-iminothiazolines (VII) have similar ultraviolet light absorption. This might be expected with the salts, for which the almost identical structures (VI) and (VIII) respectively can be written (cf. Conover and Tarbell, *loc. cit.*). The spectral similarity between the bases (V) and (VII) is surprising, and suggests that the iminothiazolines retain a more or less intact thiazole chromophore, as in the mesoionic forms (IX). In accordance with such structures, 2-iminothiazolines have been found to have a higher dipole moment (Table 2); the values found for 2-aminothiazoles are comparable with values of 1·64 D reported for thiazole and 1·75 D for 2-aminothiazole (Jensen and Friediger, *Kgl. Danske Videnskab. Selskab*, 1943, **20**, No. 2, 1; *Chem Abs.*, 1945, **39**, 2068). Mesoionic structures analogous to (IX) have been suggested in the benzothiazole series on similar evidence (Brooker, Keyes, Smyth, and Oesper, *J. Amer. Chem. Soc.*, 1941, **63**, 3192). The bicyclic bases (III) are also 2-iminothiazolines, to which the general formulation (IX) can apply.

Experimental

Halogenated intermediates will be designated as follows : chloroacetal (A), chloroacetone (B), phenacyl bromide (C), α-bromopropiophenone (D), α-bromophenylacetaldehyde diethyl acetal (E), 1-bromo-1-phenylpropan-2-one (F), 3-bromo-1-phenylpropan-2-one (G), 1-bromo-1-phenylpropan-2-one (H). Compounds (F), (G), and (H) were made by methods described by Smith and Wilson (*J.*, 1955, 1342). Bromination of acetophenone (Ward, *J.*, 1923, 2211) and of propiophenone (Pampel and Schmidt, *Ber.*, 1886, **19**, 2897; Kunckell and Dettmar, *Ber.*, 1903, **36**, 771) gave (C) (80%, m. p. 48°) and (D) (b. p. 125—130°/10 mm.) respectively; (E) (45%; b. p. 124—130°/8 mm.) was made by Bedoukian's method (*J. Amer. Chem. Soc.*, 1944, **66**, 1325). Chloroacetone diethyl ketal (b. p. 64—69°/28 mm.) was obtained in 86% yield (Ewlampiew, *Ber.*, 1929, **62**, 2387). Tetrahydro-2-thioglyoxaline (82%; m. p. 199—200°) was made by the method of *Org. Synth.*, 1946, **26**, 34. Methyl *iso*thiocyanate (*Org. Synth.*, 1941, **21**, 81) with aqueous ammonia or methylamine gave *N*-methylthiourea (65%; m. p. 117—118°) and *NN'*-dimethylthiourea (73%; 56—58°). A mixture of ethanol (50 c.c.), 2-dimethylaminoethanol (5 c.c.), and diethylcyanamide (20 g.) was heated at 45—50° for 14 hr., in a stream of hydrogen sulphide. On cooling, *NN*-diethylthiourea (18 g., 68%; m. p. 101—103°) separated (Wallach, *Ber.*, 1899, **32**, 1874, gives m. p. 101—102°).

4' : 5'-*Dihydroglyoxalino*(2' : 1'-2 : 3)*thiazolium Salts* (*Table* 3).—Molar quantities of tetrahydro-2-thioglyoxaline and α-halogenated carbonyl compounds were refluxed in ethanol for 2 hr. The colourless *products* which separated on evaporation and cooling were recrystallised from ethanol. Chloroacetone and chloroacetone diethyl ketal gave the same product. The acetal (A) reacted readily in the presence of a few drops of concentrated hydrochloric acid; (E) did not react, even in the presence of free hydrochloric acid. The colourless bases (Table 3B) usually separated when sodium hydroxide was added to aqueous solutions of the thiazolium salts. The bases were appreciably soluble in ether, and were purified by sublimation at 0·01 mm., or by recrystallisation from benzene–light petroleum (b. p. 40—60°). The two simplest bases were soluble in cold water.

Substituted 2-*Aminothiazoles* (*Table* 4).—Reaction of α-halogenated carbonyl compounds with thiourea gave compounds nos. (8)—(14) inclusive. Nos. (15), (16), and (17) were similarly obtained from *N*-methylthiourea, and (18) from *NN*-diethylthiourea. It was necessary to add a few drops of concentrated hydrochloric acid in reactions with chloroacetal. The simpler thiazolium salts were hygroscopic; the bases were obtained from the salts by addition of alkali and filtration or ether-extraction. 2-Aminothiazole (19) was a purified commercial sample.

Thiazoles (*Table* 4).—Compounds (21), (23), and (24) were made by warming α-halogenated carbonyl compounds with freshly prepared thioformamide, followed by neutralisation with ammonia and steam-distillation (cf. Erlenmeyer and Simon, *Helv. Chim. Acta*, 1942, **25**, 528). Compound (20) was made by Russel's method (U.S.P. 2,509,453), and (22) from ω-amino-acetophenone (Ohta, *J. Pharm. Soc. Japan*, 1951, **71**, 869).

TABLE 4. *Thiazoles.*

No.	Halide used	Salt	Yield (%)	M. p.	Base, m. p.
8	B	HCl	73	170—171°	38—39°
9	G	HBr	—	88—90	93—94
10	C	HBr	80	184—186	150—152
11	D	HBr	83	172—175	118—119
12	E	—	—	—	204—206 (20% yield)
13	F	HBr	55	214—216	164—166
14	H	HBr	70	215—216	143—144
15	A	HCl	Very hygroscopic		b. p. 106—107/16 mm.
16	B	HCl	65	226—227	66—69
17	C	HBr	—	149—151	136—137 (85% yield)
18	B	HCl	Syrup		b. p. 100—102/8 mm. (94% yield)
20	C	—	—	—	51—52
21	D	—	—	—	b. p. 140—142/12 mm.
22	—	—	—	—	44—45
23	F	—	—	—	b. p. 134—136/20 mm.
24	B	—	—	—	b. p. 131—132

Notes: [8] Base, m. p. 42° (Traumann, *Annalen*, 1888, **249**, 37); m. p. 44—45° (*Org. Synth.*, Coll. Vol. II, p. 31); m. p. 42°, hydrochloride, m. p. 169—171° (Lanfranchi, *Atti R. Accad. Lincei*, 1942, **3**, 776). [9] The base, m. p. 96—97°, has been made by a different method (Libermann and Moyeux, *Bull. Soc. chim. France*, 1950, 301). [10] Base, m. p. 147° (Traumann, *loc. cit.*). [11] Base, m. p. 124—125°, hydrobromide, m. p. 170—173° (Szekeres, *Gazzetta*, 1948, **78**, 681). [12] The base, m. p. 207·5—208·5°, has been made by a different method (Hurd and Wehrmeister, *J. Amer. Chem. Soc.*, 1949, **71**, 4007). [13] Base, m. p. 164—166° (Kopp, *Bull. Soc. chim. France*, 1950, 582). [14] Base, m. p. 139—140° (King and Hlavacek, *J. Amer. Chem. Soc.*, 1950, **72**, 3722). [15] Hydrochloride, m. p. 79—80°, hygroscopic (Näf, *Annalen*, 1891, **265**, 113). [16] Base, m. p. 71·5—72·5°; hydrochloride, m. p. 228° (Burtles, Pyman, and Roylance, *J.*, 1925, 588). [17] Base, m. p. 138° (Traumann, *loc. cit.*, p. 46). [18] Base, b. p. 103°/10 mm. (Ochiai and Kashida, *J. Pharm. Soc. Japan*, 1942, **62**, 97). [20] Base, prepared by another method, m. p. 52° (Popp, *Annalen*, 1889, **250**, 279); 55° (Russel, *loc. cit.*). [21] Base, b. p. 110—111°/2 mm. (Ochiai, Kakuda, Nakayama, and Masuda, *J. Pharm. Soc. Japan*, 1939, **59**, 462; b. p. 278° (Merck, G.P. 670,131). [22] Base, m. p. 45—46° (Ohta, *J. Pharm. Soc. Japan*, 1951, **71**, 869). [23] Base, b. p. 134—135°/25 mm. (Erlenmeyer and Simon, *Helv. Chim. Acta*, 1942, **25**, 528). [24] Base, b. p. 131° (Merck, *loc. cit.*; cf. Ganapathi and Venkataraman, *Proc. Indian Acad. Sci.*, 1946, **22**, *A*, 343).

TABLE 5. 2-*Iminothiazolines.*

No.	Halide used	Salt	Yield (%)	M. p.	Base, m. p.
25	A	HCl	72	235—236°	Oil
26	B	HCl	84	198—199	96—97
27	C	HBr	77	197—198	76—77
28	D	HBr	82	242—244 (dec.)	62—63
29	D	—	—	—	179 (58% yield)
30	F	HBr	60	270—272	170—173
31	—	HI	85	184—185	b. p. 104—109°/16 mm., m. p. 36—37°
32	—	HI	83	167—168	b. p. 122—123°/16 mm.
33	—	HI	85	231—233 (dec.)	Syrup

Notes: [25] Hydrochloride, m. p. 222° (Näf, *Annalen*, 1891, **265**, 116). [26] Base, m. p. 96° (Traumann, *Annalen*, 1888, **249**, 49). [27] *Base* (Found: C, 64·8; H, 6·0. $C_{11}H_{12}N_2S$ requires C, 64·7; H, 5·9%). [28] *Base* (Found: C, 65·7; H, 6·4. $C_{12}H_{14}N_2S$ requires C, 66·0; H, 6·45%); *hydrobromide* (Found: C, 47·85; H, 4·95. $C_{12}H_{14}N_2S$,HBr requires C, 48·15; H, 5·05%). [29] *Base* (Found: C, 76·95; H, 5·35. $C_{22}H_{18}N_2S$ requires C, 77·15; H, 5·3%). [30] *Hydrobromide* (Found: C, 62·75; H, 4·75. $C_{22}H_{18}N_2S$,HBr requires C, 62·4; H, 4·5%); *base* (Found: C, 77·4; H, 5·15. $C_{22}H_{18}N_2S$ requires C, 77·15; H, 5·3%). [31] Hydriodide, m. p. 175° (Näf, *loc. cit.*); m. p. 182—184°; base, b. p. 96—98°/11 mm., m. p. 44—45° (Druey, *Helv. Chim. Acta*, 1941, **24**, 226E). [32] Base, m. p. 47·5° (Traumann, *loc. cit.*, p. 44). [33] Base is an oil (Traumann, *loc. cit.*).

2-*Iminothiazolines* (*Table* 5).—Appropriate 2-aminothiazoles were refluxed for 2 hr. with methyl iodide in ethanol or propanol, to give the 2-imino-3-methylthiazoline hydriodides (31), (32), and (33). 2-Imino-3 : 4-dimethylthiazoline was obtained from the salt by addition of alcoholic potassium hydroxide and ether-extraction. Reaction of α-halogenated carbonyl compounds with *NN′*-diphenylthiourea gave compounds (29) and (30); compounds (25), (26), (27), and (28) were obtained similarly from *NN′*-dimethylthiourea. Compound (29) was weakly basic and separated from the reaction mixture as the base. The hydrobromide (30) was insoluble in water, and the base was obtained by passing dry ammonia through a chloroform solution of the salt, filtering off the ammonium bromide, and evaporating the solvent.

Physical Measurements.—Light absorption measurements (Table 1) were made with a Unicam SP. 500 spectrophotometer, with 10-mm. cells. " P.I. Rectified Spirit," which gives ⩾50% transmission of light down to 205 mμ and is cheap, was used as solvent. The absorption

of salts was measured on solutions made from either the salts or the bases, 2 drops of concentrated hydrochloric acid being added to the absorption cells. Solutions of the bases were made directly, or by adding 2 drops of 10% sodium hydroxide to cells containing solutions of the salts.

The dipole moments (Table 2) were measured by using the simple apparatus described by Bender (*J. Chem. Educ.*, **1946**, **23**, 179), and are accurate to $\pm 0{\cdot}2$ D. Concentrations of about 4 g./l. in dry benzene were employed. Compound (2) (base) gave the following dipole moments at different concentrations: 0·0106 (mole fraction), 4·23 D; 0·0077, 4·21 D; 0·0032, 4·33 D; 0·00095, 4·36 D. Evidently, there is negligible association in benzene (contrast glyoxalines, Jensen and Friediger, *loc. cit.*).

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CHEMISTRY DEPARTMENT, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM, 15.

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