246. *The Electronic Spectra of N-Heteroaromatic Systems. Part II.* Substituted Monocyclic Azones.*

By S. F. Mason.

The visible and ultraviolet absorption spectra of the monocyclic azines and some derivatives have been measured in polar and non-polar solvents. The $n \longrightarrow \pi$ bands of the azines are shifted towards the blue region by electron-donating and towards the red region by electron-accepting substituents, whilst the $\pi \longrightarrow \pi$ bands undergo bathochromic shifts with both types of substituent. The shift of the $n \longrightarrow \pi$ band of an azine on substitution is shown to be due primarily to the effect of the substituent on the energy of the lowest unoccupied benzene-like π-orbital of the azine.

The absorption bands due to $\pi \longrightarrow \pi$ transitions in the electronic spectrum of benzene and the monocyclic azines, in general, are shifted towards the red region by both electron-donating and electron-accepting substituents, as either group reduces the energy separation between the highest occupied and the lowest unoccupied π-orbital. In the spectra of the monocyclic azines, however, the absorption band due to the transition of an electron from a lone-pair orbital to a π-orbital of the ring is shifted towards the blue region by *ortho–para*-directing substituents, notably, the halogens and the methyl group, which have been the main substituents hitherto studied.[1-4] The effects of two *meta*-directing substituents (nitrile and carboxyl) and a more powerful *ortho* : *para*-directing substituent (methoxyl) upon the positions of the $n \longrightarrow \pi$ bands of the monocyclic azines have now been investigated. The visible and ultraviolet absorption spectra of the monocyclic azines and their derivatives have been measured in *cyclo*hexane, ethanol, and aqueous solution, the results being recorded in the Table and the Figs.

The band of longest wavelength in the spectra of the azines and their derivatives is relatively weak ($\varepsilon_{max.} \simeq 200$—$1000$), and it shows a pronounced blue shift on change from *cyclo*hexane to aqueous solution (Table; Fig. 1). These features suggest that the band is due to the transition of a non-bonding electron from a lone-pair orbital of a nitrogen atom to a π-orbital of the ring.[5-8] The low intensity of the band arises because the lone-pair and the π-orbitals of an azine are concentrated in different regions of space,[5] and because only the *s*-component of the *s–p* hybrid lone-pair orbital can contribute to the transition moment of a $n \longrightarrow \pi$ excitation.[8] The blue shifts of the $n \longrightarrow \pi$ bands in the electronic spectra of the azines observed on changing from *cyclo*hexane to aqueous solution are due [6,7] to the stabilisation of the ground state by hydrogen-bonding in the water, an increase in the transition energy being required to break or weaken the hydrogen bonds. In aqueous solution sufficiently acid to form the cation of the azine, the $n \longrightarrow \pi$ bands undergo further blue shifts or disappear (Table; Fig. 1), as the lone-pair electrons either bind a proton or are held more strongly in their orbital by inductive and inductomeric effects originating from a charged centre elsewhere in the cation.

In contrast to the $\pi \longrightarrow \pi$ bands of the azines, which undergo bathochromic shifts generally upon substitution, the $n \longrightarrow \pi$ bands, for the most part, move towards the blue region with *ortho–para*-directing substituents and towards the red region with *meta*-directing groups (Table; Figs. 1—3). The direction and the magnitudes of the shifts are not always apparent from the wavelength of maximum absorption, particularly for

* Part I, preceding paper.

[1] Uber and Winters, *J. Amer. Chem. Soc.*, 1941, **63**, 137.
[2] Rush and Sponer, *J. Chem. Phys.*, 1952, **20**, 1847.
[3] Halverson and Hirt, *ibid.*, 1951, **19**, 711.
[4] Stephenson, *ibid.*, 1954, **22**, 1077.
[5] Platt, *ibid.*, 1951, **19**, 101.
[6] Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14.
[7] McConnell, *J. Chem. Phys.*, 1952, **20**, 700.
[8] Orgel, *J.*, 1955, 121.

pyrazine (I) and its derivatives in *cyclo*hexane. The 0–0 vibrational peak of the $n \longrightarrow \pi$ band of pyrazine in *cyclo*hexane has the maximum intensity, but in 2-methylpyrazine the 0–1 and in 2 : 5-dimethylpyrazine the 0–2 vibrational peak is the most intense, whilst in dimethyl pyrazine-2 : 3-dicarboxylate the vibrational fine structure of the $n \longrightarrow \pi$ band is completely blurred (Fig. 1). Thus, this ester absorbs at longer wavelengths than pyrazine (Fig. 1), though the $\lambda_{max.}$ of the $n \longrightarrow \pi$ band lies at a shorter wavelength (Table). A similar effect occurs in the case of pyrimidine (II) and its 2-methoxycarbonyl derivative in *cyclo*hexane (Table). In polar solvents the wavelengths of maximum absorption give more accurately the shifts of the $n \longrightarrow \pi$ bands due to substitution, as the vibrational

FIG. 1. *The ultraviolet absorption spectra of pyrazine* —— *in* cyclo*hexane and* — · — · — *in* 5N-*sulphuric acid, and the spectra in* cyclo*hexane of* — — — — 2 : 5-*dimethylpyrazine and* . . . . . *dimethyl pyrazine*-2 : 4-*dicarboxylate.*

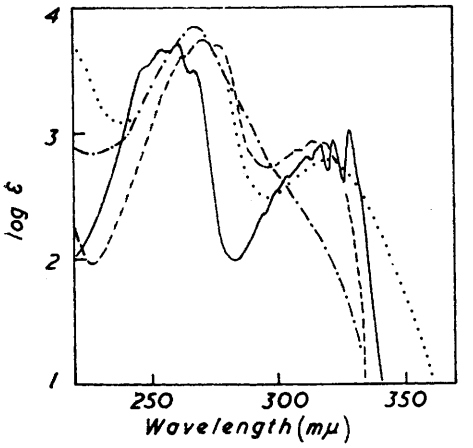
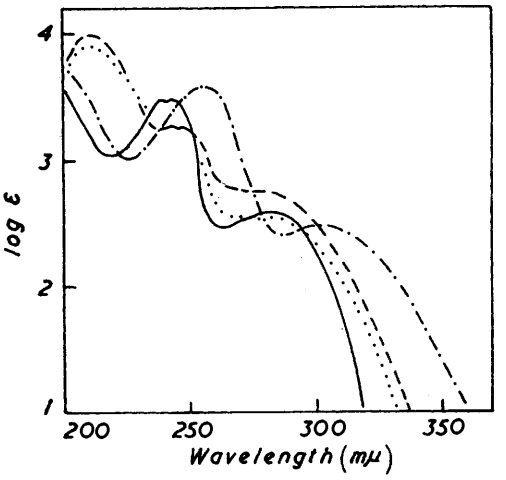
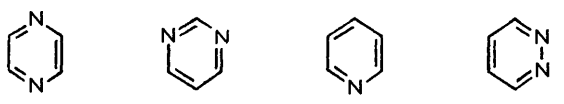


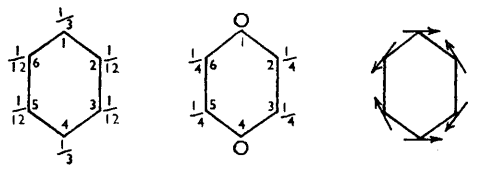
FIG. 2. *The ultraviolet absorption spectra in ethanol of* —— *pyrimidine and of* . . . . . *pyrimidine*-2-, — · — · — -4-, *and* — — — -5-*carboxylic acid.*



fine structure of the $n \longrightarrow \pi$ bands of the azines and their derivatives is completely blurred in these solvents (Fig. 2). However, pyrimidine-2-carboxylic acid absorbs at longer wavelengths than does pyrimidine in ethanol (Fig. 2), though the $\lambda_{max.}$ of the $n \longrightarrow \pi$ band lies at a slightly shorter wavelength (Table).

The shifts observed on substitution support further the assignment of the low-intensity long-wavelength bands of the azines to the transition of an electron from a lone-pair





orbital of a nitrogen atom to a π-orbital of the ring. In general, electronic charge is transferred from nitrogen to carbon in the excited state of such a transition, and, relative to the ground state, the excited state is stabilised by electron-accepting and destabilised

by electron-donating substituents, the former reducing and the latter increasing the transition energy.

In the less symmetrical azines the shift of the $n \longrightarrow \pi$ band produced by a given group varies markedly with the position of substitution. In pyrimidine a 4-methoxy- produces a larger blue shift than a 2-methoxy-group (Table), and a carboxyl group at position 4 gives a larger red shift than one at the 2- or the 5-position (Fig. 2). Similarly, in pyridine (III) and pyridazine (IV) a given substituent gives rise to larger shifts of the $n \longrightarrow \pi$ band, towards the red or the blue region depending upon the electron-accepting or -donating property of the group, when in the 4-position than when elsewhere in these rings (Table; Fig. 3).

The relative magnitudes of the shifts produced by a given group substituted at different positions in an azine appear to be governed largely by the change in the energy of the excited state of the $n \longrightarrow \pi$ transition on substitution. Suitable models for the orbital containing the promoted electron in the excited states of the $n \longrightarrow \pi$ transitions of the azines are the lowest unoccupied π-orbitals of benzene, perturbed by aza-substitution.[9]

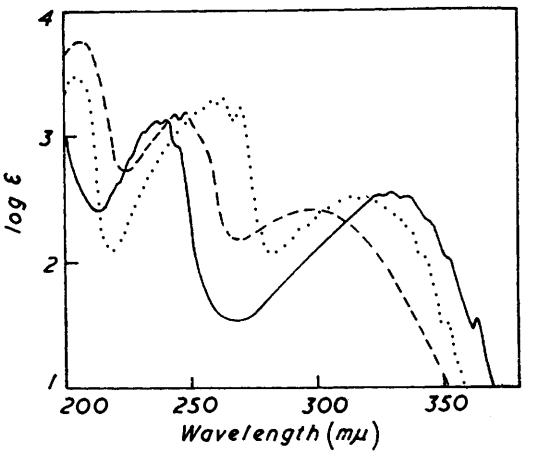


FIG. 3. *The ultraviolet spectra in* cyclohexane *of* —— *pyridazine and of* . . . . 3-, *and* — — — 4-*methoxypyridazine.*

The lowest unoccupied π-orbitals of benzene are the degenerate pair, ψ_A and ψ_B, defined in Part I; the charge distributions in ψ_A and ψ_B are given in (V) and (VI), respectively. On aza-substitution the degeneracy of ψ_A and ψ_B, in general, is removed, the energy of one orbital being lowered more than that of the other, though the forms of the orbitals, notably the charge distributions, are qualitatively preserved.

In pyridine (III) and pyrazine (I) ψ_A becomes the lowest unoccupied π-orbital, the nitrogen atoms being substituted at the 1- and the 1 : 4-positions of (V), respectively. In pyridine a non-bonding electron on promotion from the lone-pair orbital assumes a distribution given approximately by (V) in the excited state, so that $C_{(4)}$ receives the largest share of the charge transferred from the nitrogen atom. A substituent should have a greater effect upon the position of the $n \longrightarrow \pi$ band of pyridine when in the 4- than when in the 2- or 3-position, as is observed in the case of the electron-accepting nitrile group which causes red shifts in the order, 4- $>$ 3- $\geqslant$ 2-position (Table). The near equality of the red shifts in the $n \longrightarrow \pi$ band of pyridine produced by the nitrile group in the 2- and the 3-position, and the equality of the charges at those positions in (V), is probably accidental. At a higher level of approximation it can be shown [8] that more charge is transferred to the 2- than to the 3-position in the $n \longrightarrow \pi$ transition of pyridine, so that the excited state should be more stabilised by the 2- than the 3-nitrile group. However, this effect is compensated by the tighter binding of the lone-pair electrons in the ground

[9] Preceding paper.

state of 2- than of 3-cyanopyridine, owing to the inductive effect, as shown by the ionisation constants of these compounds (Table). In pyrazine each carbon atom receives the same amount of charge from the nitrogen atoms in the excited state of the $n \longrightarrow \pi$ transition, in conformity with the observation [3] that the $n \longrightarrow \pi$ band of pyrazine moves towards the blue region with nearly equal energy increments as the hydrogen atoms are successively replaced by chlorine.

In pyridazine (IV) and pyrimidine (II) ψ_B becomes the lowest unoccupied π-orbital, with the nitrogen atoms at the 2 : 3- and the 2 : 5-positions of (VI), respectively. The nodal axis through the 1 : 4-positions of (VI) is preserved in the lowest unoccupied π-orbital of pyrimidine, as it coincides with the C_2 axis of this azine. In the excited state of the $n \longrightarrow \pi$ transition of pyrimidine, therefore, charge is transferred from the nitrogen atoms only to the carbon atoms at the 4- and the 6-position. A substituent in the 2- or the 5-position of pyrimidine should not change the energy of the excited state of the $n \longrightarrow \pi$ transition, whilst in the 4-position the effect of a substituent should be large. The powerful electron-donating methoxyl group produces only a small blue shift in the $n \longrightarrow \pi$ band of pyrimidine when in the 2-position but a large shift when in the 4-position (Table). Similarly the electron-attracting carboxyl group gives a small red shift in the 2- or the 5-position of pyrimidine and a large bathochromic shift when in the 4-position (Fig. 2).

The visible and ultraviolet absorption spectra of the monocyclic azines and their derivatives in polar and non-polar solvents. Values in italics refer to shoulders or inflexions.

			$n \longrightarrow \pi$ bands		$\pi \longrightarrow \pi$ bands	
Compound	pK_a	Solvent	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$
Pyridine	5·23 [a]	C_6H_{12}	*270* [c]	*450* [c]	251	2000
		pH 9	[b]	[b]	257	2650
2-Cyano-	−0·26 ± 0·04	C_6H_{12}	*278* [c]	*340* [c]	265	2730
		pH 7	[b]	[b]	265	3790
		10N-H_2SO_4	[b]	[b]	267	7520
3-Cyano-	1·36 ± 0·03	C_6H_{12}	*279* [c]	*430* [c]	265	2230
		pH 7	[b]	[b]	265	2890
		4N-H_2SO_4	[b]	[b]	265	5130
4-Cyano-	1·90 ± 0·02	C_6H_{12}	*290*	*500* [c]	271	2840
		pH 7	[b]	[b]	275	3410
		2N-H_2SO_4	[b]	[b]	276	5710
2 : 6-Dicyano-	< −2·0	C_6H_{12}	[b]	[b]	275	3990
		pH 7	[b]	[b]	274	4900
Pyrazine	0·6 [a]	C_6H_{12}	328	1040	260	5600
		EtOH	310	860	261	6000
		pH 7	300	850	261	5900
		5N-H_2SO_4	[b]	[b]	266	7300
2-Methyl-	1·47 ± 0·04	C_6H_{12}	320	830	266	5700
		pH 7	*295*	*1120*	271	5910
		2N-H_2SO_4	[b]	[b]	276	6680
2 : 5-Dimethyl-	1·97 ± 0·02	C_6H_{12}	314	908	271	5700
		pH 7	*295*	*2000*	276	6840
		2N-H_2SO_4	[b]	[b]	285	8080
2 : 3-Dimethoxycarbonyl-	< −2·0	C_6H_{12}	319	660	268	6820
		EtOH	311	700	268	6950
		pH 7	303	740	268	7100
2 : 3-Dicarboxy-	3·57 ± 0·02	EtOH	314	690	269	6200
	0·9 ± 0·2	pH 7	*315*	*970*	281	7820
	< −2·0	pH 2·2	*305*	*812*	274	6440
		5N-H_2SO_4	*310*	*708*	270	6940
2-Methoxy-	0·75 [a]	C_6H_{12}	[b]	[b]	277	5760
		pH 7	[b]	[b]	290	5240
Pyridazine	2·33 [a]	C_6H_{12}	340	315	246	1300
		EtOH	313	303	246	1160
		pH 7	300	320	247	1090
		pH 0	[b]	[b]	238	1610
3-Methyl-		EtOH	310 [d]	400 [d]	251 [d]	1300 [d]
4-Methyl-	2·92 ± 0·01	C_6H_{12}	331	375	252	1296
		EtOH	303 [d]	350 [d]	250 [d]	1370 [d]
		pH 7	292	371	247	1440
		pH 0·7	[b]	[b]	221	6020

TABLE. (*Continued.*)

Compound	pK_a	Solvent	$n \longrightarrow \pi$ bands $\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	$\pi \longrightarrow \pi$ bands $\lambda_{max.}$ (mμ	$\varepsilon_{max.}$
3-Methoxy-	2·52 [a]	C_6H_{12}	327	326	272	1990
		pH 7	*300*	*329*	265	2330
		pH 0·5	[b]	[b]	269	2010
4-Methoxy-	3·70 [a]	C_6H_{12}	307	258	259	1560
		pH 7	*285*	*390*	254	2570
		pH 1	[b]	[b]	247	10,320
3 : 6-Dimethoxy-		C_6H_{12}	*325*	*312*	292	2500
		pH 7	[b]	[b]	284	2270
4 : 5-Dicarboxy-	3·30 ± 0·02	EtOH	345	274	266	3020
		pH 7	313	337	253	3520
		pH 1	*325*	*364*	263	3330
Pyrimidine	1·30 [a]	$C_{6\ 12}$	298	326	243	2030
		EtOH	280	373	243	2920
		pH 7	271	422	243	3210
		4N-H_2SO_4	[b]	[b]	242	5540
2-Methoxy-	< 1 [a]	C_6H_{12}	*295*	*400*	264	4180
		pH 7	[b]	[b]	267	4530
4-Methoxy-	2·5 [a]	C_6H_{12}	*270*	*274*	248	3100
		pH 7	[b]	[b]	248	3370
5-Hydroxy-		EtOH	[b]	[b]	276	5330
2-Methoxycarbonyl-	−0·68 ± 0·04	C_6H_{12}	290	370	247	1840
		pH 7	*270*	*382*	245	2300
		12N-H_2SO_4	[b]	[b]	247	4900
2-Carboxy-	2·85 ± 0·02	EtOH	277	374	246	2120
	−1·13 ± 0·05	pH 7	*275*	*410*	246	2620
		pH 0·8	*270*	*441*	240	2690
4-Carboxy-		EtOH	303	295	256	3820
5-Carboxy-		EtOH	*280*	*561*	247	1870
3 : 5 : 6-Trimethyl-1 : 2 : 4-triazine	2·85 ± 0·02	C_6H_{12}	384	520	264	5100
		pH 7	350	440	263	4700
		pH 0	[b]	[b]	245	4400
3-Amino-1 : 2 : 4-triazine	4·00 ± 0·02	C_6H_{12}	394	505	310	2730
		pH 7	*350*	*1100*	319	2820
sym-Tetrazine	< 0	C_6H_{12}	542	829	252	2150
			320	*26*		
		pH 7	510	362	255	2840
			305	*157*		
1 : 4-Dimethyl-		C_6H_{12}	562	832	273	3720
		pH 7	519	365	276	3800
1 : 4-Dicarboxy-	2·8 ± 0·2	pH 7	515	202	251	3100

[a] Quoted from Albert and Phillips, *J.*, 1956, 1294. [b] The $n \longrightarrow \pi$ band is absent or not measurable. [c] Derived by the method of ref. 4. [d] Quoted from Eichenberger, Rometsch, and Druey, *Helv. Chim. Acta*, 1954, **37**, 1298.

Pyrimidine-5-carboxylic acid absorbs at slightly longer wavelengths than the 2-isomer (Fig. 2), suggesting that in the latter the lone-pair electrons of the nitrogen atoms are bound more firmly in the ground state by the inductive effect of the substituent. However, the spectra of the pyrimidine-carboxylic acids illustrate that, in general, the position of the $n \longrightarrow \pi$ band in a substituted azine, relative to that of the parent compound, is determined primarily by the effect of the substituent upon the energy of the excited state.

The nodal axis through the 1 : 4-positions of (VI) is not preserved in the lowest unoccupied orbital of pyridazine (IV), as the C_2 axis of the molecule bisects bonds and does not run through atomic positions. Thus, a small amount of charge is transferred from the nitrogen atoms to the carbon atoms at positions 3 and 6 of pyridazine (IV) in the excited state of the $n \longrightarrow \pi$ transition, though the major transfer of charge takes place to those at positions 4 and 5. Accordingly, a given substituent in the 2-position of pyrimidine and the 3-position of pyridazine should produce a somewhat larger shift of the $n \longrightarrow \pi$ band of the azine in the latter case, whilst in the 4-positions of these azines the substituent should give rise to much larger shifts, which should be comparable with one another. It is found (Table; Fig. 3) that the methoxyl group produces red shifts of 3

and 28 mμ in the 2- and the 4-positions of pyrimidine, respectively, and of 13 and 33 mμ in the 3- and the 4-positions of pyridazine, respectively.

Less information is available on the effect of substituents on the position of the $n \longrightarrow \pi$ band of the polyazines. Chloro- and methyl groups produce the expected blue shift in the $n \longrightarrow \pi$ band of *sym*-triazine,[10] but the methyl group moves the $n \longrightarrow \pi$ band of *sym*-tetrazine towards the red region (Table). The lowest unoccupied π-orbital in *sym*-tetrazine is of the form of ψ_B, the charge distribution being confined to the nitrogen atoms. No charge is transferred from nitrogen to carbon in the $n \longrightarrow \pi$ transition of *sym*-tetrazine, and the energy of the excited state should not be changed by substituents. The red shifts produced by methyl and carboxyl groups may be due to a modification, consequent upon substitution, of the ground-state interaction between the four lone-pair orbitals.[9]

Some features of the first $\pi \longrightarrow \pi$ band of the substituted azines may be accounted for qualitatively by the theory of Sklar,[11] Forster,[12] Platt,[13] and Murrell and Longuet-Higgins,[14] on the assumption that this band corresponds to the 260 mμ band of benzene perturbed by the ring nitrogen and the exocyclic substituents. The intensity changes in the 260 mμ band of benzene, following substitution, can be derived [11-13] by adding vectorially, according to the scheme of (VII), migration moments [11] or spectroscopic moments [13] characteristic of the substituents. The wavelength shift of the band on the poly-substitution of benzene may be obtained [12] from the intensity increment and an additional parameter. The spectroscopic moments [13] of the substituents studied in the present work are: OH 23, OMe 31, Me 7, CN −19, CO_2H −28, and aza-N −38.

The intensity of the first $\pi \longrightarrow \pi$ band of the unsubstituted azines is explained only qualitatively by the appropriate vector addition of the spectroscopic moment of the ring-nitrogen atom according to (VII). Quantitatively the intensities of the first $\pi \longrightarrow \pi$ band in pyrimidine and pyridazine, and in pyrazine and *sym*-tetrazine, should be equal, but the 1 : 2-diaza-compound of each pair absorbs with the lower intensity (Table). Qualitatively, however, the intensity and wavelength changes follow the order expected in both the azines and their derivatives. In the 2- and the 3-position of pyridine the nitrile group produces smaller increases in the wavelength and the intensity of maximum absorption than when it is in the 4-position (Table). The intensity of the $\pi \longrightarrow \pi$ band of pyrimidine is reduced and moved very little towards the red region by a carboxyl group at position 2 or 5, but at the 4-position the group enhances the intensity and gives a large red shift (Fig. 2). Conversely a hydroxyl or methoxyl group in the 2- or the 5-position of pyrimidine gives rise to a large bathochromic shift and intensity increase, but with a methoxyl group at position 4 such changes are small (Table). Similarly, the effects of substituents upon the position and the intensity of the $\pi \longrightarrow \pi$ band of pyridazine are qualitatively those expected from the signs and the magnitudes of the spectroscopic moments of the substituents, but in pyrazine- and *sym*-tetrazine-dicarboxylic acids the expected diminution in the intensity of the $\pi \longrightarrow \pi$ band is not observed (Table).

Experimental

Absorption Spectra.—These were measured with Hilger Uvispek Quartz Spectrophotometers, the solvents listed in the Table being used.

Ionisation Constants.—These were determined by potentiometric titration of 0·1—0·01M-solutions, a Cambridge pH meter being used with glass and calomel electrodes for compounds with pK_a values >1. pK_a values <1 were determined spectrophotometrically at 0·0001M.

Materials.—The unsubstituted azines were as in Part I.[9] 5-Hydroxypyrimidine and pyrimidine-4- and -5-carboxylic acid were kindly provided by Dr. J. F. W. McOmie,[15] pyrimidine-

[10] Hirt, Halverson, and Schmitt, *J. Chem. Phys.*, 1954, **22**, 1148.
[11] Sklar, *ibid.*, 1942, **10**, 135.
[12] Forster, *Z. Naturforsch.*, 1947, **2a**, 149.
[13] Platt, *J. Chem. Phys.*, 1951, **19**, 263.
[14] Murrell and Longuet-Higgins, *Proc. Phys. Soc.*, 1955, **68**, *A*, 329.
[15] Boarland and McOmie, *J.*, 1952, 3716.

2-carboxylic acid and its methyl ester by Dr. A Holland,[16] 4-methyl-, 3- and 4-methoxy-, and 3 : 6-dimethoxy-pyridazine by Dr. K. Eichenberger and Dr. J. Druey,[17] and 3 : 5 : 6-trimethyl-1 : 2 : 4-triazine by Dr. R. Metze.[18] Pyrazine-2 : 3-dicarboxylic acid and its dimethyl ester were prepared by Gabriel and Sonn's method,[19] and pyridazine-4 : 5-dicarboxylic acid by Gabriel's method.[20] 1 : 4-Dimethyltetrazine and tetrazine-1 : 4-dicarboxylic acid were prepared by the methods of Curtius, Darapsky, and Müller,[21] and 3-amino-1 : 2 : 4-triazine by Erickson's method.[22]

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[16] Holland, *Chem. and Ind.*, 1954, 786.
[17] Eichenberger, Rometsch, and Druey, *Helv. Chim. Acta*, 1954, **37**, 1298; Staehelin, Eichenberger, and Druey, *ibid.*, 1956, **39**, 1741.
[18] Metze, *Ber.*, 1955, **88**, 772.
[19] Gabriel and Sonn, *Ber.*, 1907, **40**, 4850.
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[21] Curtius, Darapsky, and Müller, *Ber.*, 1907, **40**, 84; 1915, **48**, 1614.
[22] Erickson, *J. Amer. Chem. Soc.*, 1952, **74**, 4706.