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VIBRATIONAL AND ELECTRONIC SPECTRA OF AROMATIC SIX-MEMBERED AZACYCLIC COMPOUNDS

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INTRODUCTION

Six-membered aromatic azacyclic compounds occur as structural units in a large number of more complicated compounds having important and diverse applications. These molecules are present in biologically active substances[1,2]. For example, thymine and cytosine, component parts of deoxyribonucleic acids (DNA)[3-5], are pyrimidine derivatives. Pyrazine derivatives are widely used in the synthesis of medicinal preparations and dyes[6]. Although pyridine and the diazines have been known for a long time, free symmetrical triazine was discovered only in 1953, by Grundmann and Kreutzberger[7]; its physical and chemical properties were soon studied in detail, and have been described in a review by Finkel'shtein and Boitsov[8]. Apart from their varied practical applications, these substances are of great interest also for the further development of the theory of chemical structure.

One of the chief physical methods for studying molecular structure is the application of spectroscopy, and during recent years a large amount of theoretical and experimental research has been done on the vibrational and electronic spectra of six-membered aromatic nitrogen heterocycles. The present review is devoted to their interpretation and systematisation. It consists of two parts: the first discusses the vibrational spectra of pyridine, and three diazines, triazine, and tetrazine; and the second part gives an analysis of the absorption and luminescence spectra of the same compounds. The review covers all the important experimental papers and calculations completed up to 1966.

I. VIBRATIONAL SPECTRA

1. Geometrical Structure of Azines and Classification of Vibrations

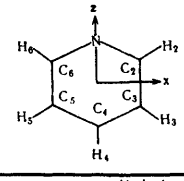
The replacement of one or more carbon atoms in the benzene ring by nitrogen atoms results in a change in the force field and distortion of the ring from the regular hexagon form. All azine molecules are planar. The bond lengths and valency angles have been determined by various physical methods—X-ray examination, electron diffraction, microwave spectroscopy, study of the rotational structure of the electronic spectra—and a complete list of all the geometrical parameters of the azines has been compiled by Berezin[9] (Tables 1 and 2). Experimental data on the geometrical structure of pyridazine are lacking.

The coordinate axes indicated in Tables 1 and 2 have been used in the classification of the normal vibrations of azines according to symmetry types. The symmetry group and the types of vibration are given below for each of the molecules.

Pyridine C_{2v}, $10A_1 + 3A_2 + 9B_1 + 5B_2$.
Pyrimidine C_{2v}, $9A_1 + 2A_2 + 8B_1 + 5B_2$.
Pyridazine C_{2v}, $9A_1 + 4A_2 + 8B_1 + 3B_2$.
Pyrazine D_{2h}, $5A_g + 2A_u + 4B_{1g} + 2B_{1u} + B_{2g} + 4B_{2u} + 2B_{3g} + 4B_{3u}$.
1,3,5-Triazine D_{3h}, $3A_1' + 2A_2' + 2A_2'' + 5E' + 2E''$.
1,2,4,5-Tetrazine D_{2h}, $4A_g + A_u + 3B_{1g} + 2B_{1u} + 3B_{2u} + 2B_{2g} + 3B_{3u}$.

Vibrations of the symmetry types A_1, B_1, A_g, B_{1g}, B_{2u}, B_{3u}, A_1', A_2', and E' are planar, whereas the remaining vibrations are non-planar. The vibrations E' and E'' are doubly degenerate. All vibrations of molecules with symmetry C_{2v}, vibrations having the subscript g, and the vibrations A_1, E', and E'' are active in the Raman spectra. The vibrations A_1, B_1, and B_2, vibrations having the subscript u, and the vibrations A_2'' and E' are active in the infrared spectra. Vibrations of types A_u and A_2' are forbidden by the selection rules, and are inactive in vibrational spectra of both types.

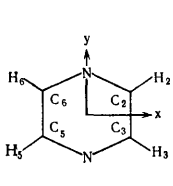
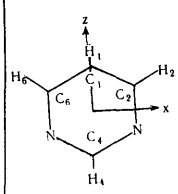
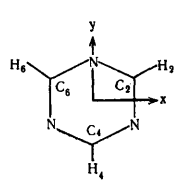
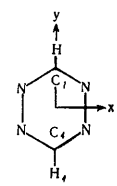
TABLE 1. Bond lengths (Å) and valency angles in the pyridine molecule according to various authors*.



Bonds and angles	Method					
	electron diffraction (Ref. 10)	microwave spectrum (Ref. 12)	microwave spectrum (Ref. 14)	microwave spectrum (Ref. 12)	electron diffraction (Ref. 14)	calc. (Ref. 15)
C_2-H_2	1.090	1.080	1.080	1.085	1.078	1.092
C_3-H_3	1.090	1.080	1.080	1.080	1.078	1.080
C_4-H_4	1.090	1.080	1.080	1.075	1.078	1.080
$N-C_2$	1.370	1.350	1.355	1.342	1.377	1.355
C_2-C_3	1.405	1.390	1.390	1.391	1.377	1.397
C_3-C_4	1.405	1.390	1.390	1.398	1.377	1.397
C_6NC_2	119°	117°	115°30′	116°42′	—	114°46′
NC_2C_3	121°	123°	—	124°	—	125°04′
$C_2C_3C_4$	121°	119°48′	—	118°36′	—	118°23′
$C_3C_4C_5$	121°	117°24′	—	118°06′	—	118°20′
NC_2H_2	—	—	—	115°44′	—	114°18′
$C_2C_3H_3$	—	—	—	120°16′	—	120°38′
$C_3C_4H_3$	—	—	—	120°17′	—	120°30′
$C_4C_3H_3$	—	—	—	121°07′	—	121°07′
$C_3C_4H_4$	—	—	—	120°57′	—	120°50′

* References 11 and 13 appear to be omitted from the text; the former refers to an electron diffraction study of pyridine; the latter refers to the study of the microwave spectrum of pyridine (Ed. of Translation).

TABLE 2. Bond lengths (Å) and valency angles in pyrazine, pyrimidine, 1,3,5-triazine, and 1,2,4,5-tetrazine.

Bonds and angles	Pyrazine			Pyrimidine*	1,3,5-Triazine		1,2,4,5-Tetrazine*
							
	electron diffraction (Ref. 10)	X-ray diffraction (Refs. 17,18)	rotational structure of ultraviolet spectrum (Ref. 19)	X-ray diffraction (Ref. 16)	X-ray diffraction (Ref. 20)	Raman rotational spectrum (Ref. 21)	electron diffraction (Ref. 22)
$C_1—C_2$				1.38			
$C_2—C_3$	1.39	1.378	1.395	1.41			
$C_2—N$				1.35			
				1.36			
C—N	1.35	1.334	1.341	1.33	1.319	1.338	1.334
				1.34			1.321
N—N							
C—H	1.09	1.05	1.085		1.00	1.084	
CNC	120°	115°66′	116°	115°12′	113°12′	113°12′	
				115°06′			
NCN				128°12′	126°48′	126°48′	127°22′
CCN	120°	122°24′	122°	122°30′			
				122°42′			
CNN							115°57′
CCC				116°18′			
NCH		116°54′					
CCH		120°18′					

* The numbering of the atoms in the formula does not correspond to the standard numbering for nomenclature purposes (Ed. of Translation).

2. Experimental Data on Vibrational Spectra and Their Interpretation

(*a*) Pyridine. Many investigations have been made of the Raman spectrum of pyridine [23-30], in all of which the intensity was merely estimated qualitatively or on a denary scale. Depolarisation measurements were made [23,24] only for a very few lines, and the results did not give the true depolarisations. Only one paper [31] has given quantitative data for standard intensities and true depolarisation measurements, together with the Raman line widths.

Determinations have been made of the infrared spectra of pyridine vapour [32,27] and liquid pyridine [24,27,33-35]. Interpretation of the vibrational spectra became considerably more reliable after examination of the Raman and infrared spectra of pentadeuteriopyridine [24], and of 4-mono- and 2,6- and 3,5-di-deuteriopyridines in liquid and vapour states [29]. The infrared spectrum of pyridine vapour itself was also obtained in the latter work [29]. The infrared spectra of the above two dideuteriopyridines in both states have subsequently been examined in detail [36]. In another case the infrared spectra of the three monodeuteriopyridines were obtained [37].

Before the problem of the normal vibrations of pyridine and its deuterio-derivatives was solved, the interpretation of the vibrational spectra had been based on the product rule for the frequencies of isotopic molecules, selection rules, comparing the spectra of pyridine and deuteriopyridines with thoes of benzene and deuteriobenzenes, and comparing the infrared and Raman spectra of pyridines in liquid and vapour states [24,29]. A theoretical calculation [36] of the vibration frequencies of pyridine and pentadeuteriopyridine using the force constants of benzene did not give satisfactory results. A complete calculation of all the vibration frequencies of pyridine and the deuteriopyridines has been reported for the first time [38]. A solution has been obtained [39] to the problem of the non-planar vibrations of pyridine and the deuteriopyridines, with a determination of the system of force constants, and also for the planar vibrations [40]. A fresh calculation has been made [41] of the planar vibration frequencies of pyridine and pentadeuteriopyridine using the force constants of benzene. The frequencies and modes of vibration of 4-deuteriopyridine and of 2,6- and 3,5-dideuteriopyridines, together with the atomic displacements in all 27 vibrations of pyridine itself, these three deuterio-derivatives, and pentadeuteriopyridine, have been calculated [42] using the force constants of benzene. The Urey–Bradley potential function has been applied [43] to the calculation of the frequencies of the same molecules. An advantage of such a function is the smaller number of force constants involved, compared with the complete quadratic potential function in the valency–force system of vibrational coordinates. However, as discussions during recent years have shown, this advantage is ineffective, since the Urey–Bradley force constants have no real physical meaning. It is not suprising, therefore, that sufficiently good agreement was not achieved [43] between calculated and experimental frequency values.

The most complete interpretation of the vibrational spectra of pyridine and the deuteriopyridines has been given by Berezin [39,40,9]. Its reliability is based on a complete solution of the converse vibrational problem—calculation of the vibrational modes and the atomic displacements during vibration—and is confirmed by good adherence to the product rules and Sverdlov's addition rules for the squares of frequencies [44] and the frequencies themselves [45] for isotopic molecules and Brodersen and Langseth's complete isotopic rule [46].

(*b*) Pyrimidine. The experimental data are far more limited than in the case of pyridine. The Raman spectra of liquid pyrimidine have been obtained[47,48], and an interpretation has been suggested[48] for the spectra. The absorption curve has been given[49] over the range 750–2000 cm^{-1}. Separate narrow portions of the infrared spectrum have been studied[50–53], and a more detailed investigation of the infrared spectrum has been made[47]. Several vibration frequencies have been obtained from the phosphorescence spectrum recorded at a low temperature[54]. The frequencies and vibrational modes have been calculated, and the vibrational spectra interpreted[55]. The frequencies and band intensities of the non-planar vibrations of pyridine, pyrimidine, and their methyl derivatives have been compared[56] with the corresponding frequencies and intensities for benzene and its substituted derivatives. This comparison introduced certain changes into the previously accepted interpretation of individual bands, but we are unable to go into these details.

(*c*) Pyridazine. The Raman and infrared spectra of liquid pyridazine have been obtained[47,48]. In the first of these papers[47] only five frequencies were found in the Raman spectrum, while the infrared spectrum was examined only in the range $\nu > 650$ cm^{-1}. The second paper[48] reported a more detailed study of both spectra, the infrared spectrum beginning at 370 cm^{-1}, and an assignment of frequencies to symmetry types was suggested. The whole system of fundamental frequencies has been calculated[57].

(*d*) Pyrazine. The Raman and infrared spectra have been obtained[47]. Another paper[48] reports both infrared and Raman spectra of liquid pyrazine, together with the infrared spectrum of its vapour. Several vibration frequencies have been determined from the low-temperature phosphorescence spectrum[58,59]. None of these investigations gives a complete system of fundamental frequencies, but they mutually complete the vibrational spectrum.

The first theoretical interpretation was based[48] on selection rules (rule of mutual exclusion), intensities and depolarisations, and comparison with the spectra of benzene and pyridine. This approach does not solve the problem, but it serves as an important prerequisite for a theoretical calculation. The first such calculation[60] used the force constants of benzene, and did not give satisfactory agreement between calculated and experimental frequencies. New calculations have been made[61,62] of the frequencies of non-planar and planar vibrations. The most complete solution of the problem of non-planar and planar vibrations with the full quadratic potential function has been accomplished[63,64] by calculation of the derivatives of the frequencies with respect to the force constants. Nevertheless, the interpretation given in these papers cannot be regarded as definitive, since the number of force constants to be determined exceeded the number of frequencies. In this case neither the force constants themselves nor the frequency assignments were determined unambiguously.

New opportunities for theoretical calculations were opened up by the determination of the vibrational spectra of the deuteriopyrazines. The Raman spectra[65] of pyrazine and tetradeuteriopyrazine in the liquid state and the infrared spectra of the latter compound in both liquid and vapour states permitted a detailed discussion of the various ways in which individual frequencies could be assigned taking into account the product rule and the assignment of combination frequencies. In an investigation[66] of the infrared spectra of pyrazine, *cis*-di-, and tetra-deuteriopyrazines in vapour and solid states, over the wide range 400–4000 cm^{-1}, frequency assignment was partly based on such new data as measurements of the dichroism of oriented crystals, analyses of rotational band envelopes, and polarisation measurements. These characteristics enabled pyrazine frequencies of symmetry types B_{1g}, B_{2g}, and B_{3g}, which were inactive in the infrared spectrum, to be determined. Finally, some additional information on the vibrational frequencies of pyrazine could be obtained from an analysis of the vibrational structure of its ultraviolet absorption spectrum[67,68] and a comparison of the frequencies of the ground and excited electronic states. In spite of such diverse approaches to the problem, a final solution was not achieved, since the interpretations of different authors did not agree among themselves.

A fresh theoretical calculation of the planar vibration frequencies of pyrazine, *cis*-di-, and tetra-deuteriopyrazine has been made[69] both with a valence-force potential function and with the Urey–Bradley potential function. The fact that both methods yielded the same frequency assignments is reassuring. Nevertheless, in many cases this assignment contradicts the results of other authors. It is obviously an urgent task to obtain the Raman spectrum of dideuteriopyrazine and to make fresh theoretical calculations in which all the isotopic rules are taken into account.

(*e*) 1,3,5-Triazine. The first determination of the Raman and infrared spectra was accompanied[70] by the first suggested assignment of the frequencies. Other analyses of these spectra were made[71,72], but in the most complete investigation of both spectra for both the triazine and the corresponding trideuteriotriazine[73] the infrared spectra were obtained for both liquid and gaseous states, and an approximate calculation was also made of the vibration frequencies. The planar vibration frequencies for both compounds have been calculated[74] by means of the Urey–Bradley potential function, but the resulting frequency assignments showed poor agreement with the addition rule for the frequencies of isotopic molecules. An attempt has been made[75] to solve the converse vibrational problem by determining 19 force constant, but such a solution cannot be regarded as complete. Solutions of the problems concerning the non-planar and planar vibrations have been obtained for both molecules[63,64] with the force constants of pyridine as zero-approximation constants.

(*f*) 1,2,4,5-Tetrazine. Infrared spectra have been investigated[76] for the symmetrical tetrazine and its mono- and di-deuterio-derivatives. Those of tetrazine itself in the range 700–3070 cm^{-1} were recorded for three states—the frozen solid phase, a solution in carbon tetrachloride, and the vapour—but those of the deuterio-derivatives were obtained not for the isotopically pure substances but for mixtures containing various percentages of tetrazine and mono- and di-deuterio-tetrazines, which made interpretation extremely difficult. As far as we are aware, the Raman spectrum of 1,2,4,5-tetrazine has not been obtained, but several frequencies, which should be active in the Raman spectrum, appear as weak lines in the infrared spectrum, thus infringing the rule of mutual exclusion. Some additional results for the assignment of frequencies have been obtained from analysis of the vibrational structure of the ultraviolet absorption bands[77,78] of symmetrical tetrazine and dideuteriotetrazine. The above limited spectroscopic data, together with the product rule and a solution of the problem of the normal vibrations of 1,2,4,5-tetrazine[64], has enabled an interpretation of its

TABLE 3. Interpretation of vibrational spectra of azines.

	Benzene		Pyridine			Pyrimidine			Pyridazine			Pyrazine			1,3,5-Triazine			1,2,4,5-Tetrazine	
sym.* type	Wilson No.	ν, cm^{-1}	sym. type	Raman ν, cm^{-1}	infrared ν, cm^{-1}	sym. type	Raman ν, cm^{-1}	infrared ν, cm^{-1}	sym. type	Raman ν, cm^{-1}	infrared ν, cm^{-1}	sym. type	Raman ν, cm^{-1}	infrared ν, cm^{-1}	sym. type	Raman ν, cm^{-1}	infrared ν, cm^{-1}	sym. type	infrared ν, cm^{-1}
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
E_u^{-I}	20b	3080	B_1	3090 (2)	3080 (v.s.)	B_1		3095 (m.)	A_1	3063 (5p)	3062 s.	B_{3u}		3070 (v.s.)	E'		3056 (s.)		
E_u^{-II}	20a	3080	A_1	3069 (0)		A_1	3083 (1)								E'		3056 (s.)	B_{3u}	3070 (m.)
A_{1g}	2	3062	A_1	3054 (8; 0.36)	3055 (s.)	A_1	3048 (10p)	3047 (s.)	A_1	3043 (6p)		A_g	3060 (9p)		A_1'	3042 (10p)			
B_{1u}	13	3060	A_1	3054 (8; 0.36)	3055 (s.)	A_1	3001 (1)		B_1		3075 (v.s.)	B_{3u}	(3090)					A_g	3040 (w.)
E_g^{+II}	7b	3047	B_1	3035 (0)	3036 (v.s.)	B_1				3043		B_{1g}	3060 (9p)						
E_g^{+I}	8a	1596	A_1	1580 (5; дп?)	1583 (v.s.)	A_1	1566 (5)	1570 (v.s.)	A_1	1578 (2)	1572	A_g	1584 (3p.)		E'	1555 (3dp)	1556 (s.)	A_g	(1489)
E_g^{+II}	8b	1596	B_1	1572 (5)	1572 (m.)	B_1	1566 (5)	1570 (v.s.)	B_1	1565 (3)	1565 (s.)	B_{1g}	1523 (3dp)		E'	1555 (3dp)	1556 (s.)	B_{1g}	(1543)
E_u^{-II}	19a	1485	A_1	1480 (2; 0.26)	1482 (s.)	A_1	1466 (1)	1467 (s.)	A_1	1446 (1)	1444 (s.)				E'	1410 (2dp)	1410 (v.s.)		
E_u^{-I}	19b	1485	B_1	1437 (0)	1441 (v.s.)	B_1	1398 (0)	1402 (v.s.)	B_1		1414 (s.)	B_{2u}		1413 (v.s.)	E'	1410 (2dp)	1410 (v.s.)	E_{2u}	1434 (w.)
A_{2g}	3	1326	B_1	1288 (1)	1296 (v.s.)	B_1	(1304)	(1304)	A_1	1283 (3)	1283 (s.)	B_{1g}	(1350)		A_2'	1278 (00)		B_{1g}	1278 (w.)
B_{2u}	14	1310	B_1	1224	1226	B_1	1227 (3)	1227 (s.)	B_1	1239 (2)		B_{3u}		1346 (v.w.)					
E_g^{+I}	9a	1178	A_1	1218 (5; 0.74)	1217 (s.)	A_1	1137 (4p)	1141 (s.)	A_1	1158 (6p)	1160 (m.)	A_g	1232 (2p)		E'	1176 (2dp)	1174 (m.)		
E_g^{+II}	9b	1178	B_1	1145 (1; dp)	1148 (s.)	B_1	1145 1160 (1)	1161 (s.)				B_{3u}		1490 (s.)	E'	1176 (2dp)	1174 (m.)	B_{3u}	1187 (v.s.)
E_u^{-I}	10b	1037	B_1		1081	B_1		1071 (s.)	A_1	1063 (8p)	1063 (s.)				A_2'		1068 (w.)	B_{2u}	1085 (m.)
E_u^{-II}	18a	1037	A_1	1068 (1)	1068 (s.)		1074 (8)		B_1		1052 (m.)	B_{3u}		1135 (s.)				B_{3u}	1106 (v.s.)
B_{1u}	12	1010	A_1	1030 (10, 0.05)	1030 (v.s.)	A_1	1053 (8p)	1055 (m.)	B_1	1006 (2)	1009 (v.s.)	B_{1u}		1021 (v.s.)	A_1'	1132 (8p)	1132 (v.w.)	B_{2u}	1200 (v.s.)
A_{1g}	1	992	A_1	991 (10; 0.05)	991 (v.s.)	A_1	991 (10p)	991 (s.)	A_1	962 (7p)	964 (s.)	A_g	1015 (9p)		A_1'	992 (7p)		A_g	990 (v.w.)
E_u^{+II}	17a	970	A_2	979 (1)	981 (w.)	A_2	870 (0)		B_2		987 (w.)	A_u	(950)		E''		830 (m.)		
B_{2g}	5	985	B_2	933 (1)	938 (v.w.)	B_2		980 (w.)	A_2	936 (1)		B_{3g}	753 (1)		A_2''		925 (v.w.)	B_{3g}	925 (m.)
E_g^{-I}	10a	849	A_2	883 (2)	883 (v.w.)				A_2	906 (1)		B_{2g}	925 (1dp)			(m.)			
E_g^{-II}	10b	849	B_2	883 (2)	883 (v.w.)	B_2	814 (0)	806 (s.)										B_{1u}	800 (v.s.)
B_{3g}	4	703	B_2	748 (0)	749	B_2	724 (1)	722 (v.s.)	A_2	751 (1)		B_{3g}	703 (3dp)		A_2''		737 (s.)		
A_{2u}	11	671	B_2	705 (0)	703 (v.s.)	B_2	679 (6)	679 (m.)	B_2		760 (v.s.)	B_{1u}		786 (v.s.)				B_{3g}	(775)
E_g^{+II}	6b	606	B_1	652 (5; 0.84)	653 (w.)	B_1		667 (s.)	A_1	661 (2dp)	664 (m.)	B_{1g}	641 (1)		E'	676 (6dp)	657 (s.)	B_{1g}	(679)
E_g^{+I}	6a	606	A_1	602 (2; 0.75)	604 (s.)	A_1	623 (2 dp)	624 (v.s.)	B_1	619 (2dp)	619 (v.s.)	A_g	609 (1)		E'	676 (6dp)	657 (s.)	A_g	737?
E_u^{+I}	16b	405	B_2	404 (1dp)	405 (s.)	B_2		344 (v.s.)	A_2	421 (1)		B_{1u}		417 (v.s.)	E''	340 (4dp)		B_{1u}	(340)
E_u^{+II}	16b	405	A_2	377		A_2	394 (2)		B_2	367 (2dp)	370 (s.)	A_u	(400)		E''	340 (4dp)		A_u	(319)
												B_{2u}		1063 (v.s.)	E'		830 (m.)		

* sym. = symmetry; v.s. = very strong; s. = strong; m. = medium; w. = weak; v.w. = very weak; p. = polarised; dp. = depolarised.

vibrational spectrum to be obtained which must be regarded as tentative. To refine this, the Raman spectrum must be obtained, and fresh calculations made.

We have been able to deal only briefly with the evolution of our knowledge of the vibrational spectra of the azines, without discussing individual frequencies. The results of comparing all the spectra and calculations of the frequencies and modes of the vibrations together with the atomic displacements during vibrations are listed in Table 3, which contains 27 fundamental frequencies for pyridine, 24 for each of the diazines, and 21 and 18 for symmetrical triazine and tetrazine. In Table 3 the frequencies of all the azines are compared among themselves and with those of benzene, for which the generally accepted Wilson numbers[79] are indicated. The symmetry types are given for each molecule. Table 3 permits the variation in frequencies to be traced in a series of azines. Unfortunately, owing to lack of space, we have not included the frequencies of the deuterioaxines in Table 3.

3. General Characteristics of the Force Field in Azine Molecules

It has now been established that vibrational spectra provide a great deal of information about the force fields in molecules. Indeed, the complete solution of the vibrational problem, with the establishment of a set of force constants and weighting coefficients [sic], permits conclusions to be drawn concerning the distribution of forces in a molecule and the variations in the force field occurring in series of compounds. Thus it follows from a comparison of these characteristics for benzene and pyridine that replacement of a carbon by a nitrogen atom leads to a breakdown in the equivalence of the bonds forming the ring. The carbon–nitrogen bond is more elastic than the remaining cyclic bonds or the carbon–carbon bond in benzene. The angles also become more elastic. The carbon–nitrogen bond exerts a greater resistance to displacement out of the plane of the ring than does the carbon–carbon bond. At the same time the interactions of non-adjacent structural units

of the ring are weakened in comparison with the corresponding interactions in benzene, which can be explained qualitatively by the greater degree of localisation of the π-electrons in pyridine. The CNC angle is, like the carbon–nitrogen bond, exceptional in its properties, which is obviously connected with the role of the lone pair of electrons on the nitrogen atom. The result is that the interaction of adjacent bonds in the ring is weaker if their common atom is nitrogen. The interaction of non-adjacent internal angles among themselves and with the external angles becomes weaker as the number of nitrogen atoms in the ring increases. These conclusions have been reached predominantly on the basis of an analysis of systems of weighting coefficients[9]. Comparison of them with other characteristics of the molecules (bond lengths and energies, atomic charges, bond orders) indicates a correlation with these parameters. It is especially interesting that a correlation has been established between the properties of the weighting coefficient of each nitrogen ring and its aromaticity, as well as with the Hammett σ-constants[9].

4. General Features of Vibrational Spectra of Azines

A comparative analysis of the vibrational spectra of benzene and the azines, together with calculations of the vibrational modes and the atomic displacements, enable the following generalisations to be made

(*a*) On passing from benzene to the nitrogen rings, the degeneracy is eliminated from ten degenerate vibrations of benzene. Each doubly degenerate frequency is split into two components (with the exception of 1,3,5-triazine). The magnitude of the splitting is small, but depends on the number and positions of the nitrogen atoms.

(*b*) Many vibrations of the nitrogen rings and the benzene ring are similar in mode and atomic displacements. The actual frequencies are also close to one another, and can be subdivided into the following groups (cm^{-1}).

1600–1500.	Planar stretching–deformation vibrations with varying participation of the bonds forming the ring, and of its external and internal angles. These lines are intense in both Raman and infrared spectra.
1500–1400.	Planar deformation–stretching vibrations with CCH angles predominantly involved. They are characterised by high intensity in the infrared spectrum.
1200–1060.	Planar stretching–deformation vibrations of the carbon–nitrogen skeleton.
1010–960.	Planar stretching vibrations of the ring bonds. They are distinguished by high intensity in the Raman and infrared spectra.
740–600.	Planar vibrations of the internal angles of the ring. The intensities vary in the series of nitrogen rings.
760–670. 420–320.	Non-planar vibrations of the carbon–carbon, carbon–nitrogen, and nitrogen–nitrogen bonds. They relate partly also to non-planar vibrations of carbon–hydrogen bonds. Frequencies in the first of these ranges are usually distinguished by high intensity in the infrared spectra

Besides the classification of frequencies according to vibrations of bonds and angles individual azines can be identified[80–88] from sets of frequencies However, discussion of this analytical problem lies outside the scope of the present paper.

II. ELECTRONIC SPECTRA

A. EXPERIMENTAL WORK ON ABSORPTION AND EMISSION SPECTRA

1. Pyridine

(*a*) Spectra of vapour. The early investigators[89–92] of the spectra of the vapour encountered difficulties in the range 3000–2400 Å in arranging the large number of lines observed in electronic–vibrational progressions having a common origin. Vibrational analysis of the bands showed[93] that two electronic transitions are apparent in this range, with frequencies of the 0–0 bands at 34 769 and about 38 350 cm^{-1}. Two band systems correspond to them—a very weak system, masked by a stronger diffuse system in the short-wavelength part of the spectrum—the first of which has no analogue in the spectrum of benzene, whereas the second system is analogous to the absorption of benzene in the region of 2600 Å. The similarity between the spectrum of pyridine in the region of 2500 Å and the absorption of benzene at 2600 Å was noted by another worker[94]. Extension of the spectral range to 1500 Å revealed[95] two new ranges of absorption, at 47 800–54 500 and 54 500–64 000 cm^{-1}. Estimates were made in this paper also of the oscillator strengths. Subsequent analysis[96] over the range 1800–1600 Å showed the presence of at least three band systems—sharp, diffuse, and continuous—so that the absorption spectrum contains five band systems—two sharp systems at 34 769 and 54 000 and three diffuse systems at 39 000, 49 769, and 56 405 cm^{-1}—and comparison of this spectrum with those of other aromatic compounds[97] indicates the possibility of using it for analytical purposes.

(*b*) Spectra of solutions. To determine the nature of the absorption spectrum and of the individual bands, it was important to investigate solvent effects on the spectrum. The spectrum of a solution in heptane was first studied[98], and subsequently that of an aqueous solution[99]. The spectra in many solvents showed[92,95,100,101] that the absorption maxima shift little, while the intensities increase in the sequence—hydrocarbons, water, alcohols, acids—a generalisation which has been used[102] to determine the acid–base properties of various substances with respect to pyridine. The absorption at 34 769 cm^{-1} disappears in polar solvents[100].

2. Diazines

(a) Spectra of vapours. The early investigations of the near ultraviolet absorption of pyrimidine[103], pyridazine, and pyrazine[104] showed the presence of two band systems—diffuse and sharp—in each case. The former corresponds to the absorption of benzene at 2600 Å, while the latter occurs at longer wavelengths. Analyses have been made of the vibrational structure of the sharp (3200 Å)[19,105–107] and diffuse[106] band systems of pyrazine.

TABLE 4. Interpretation of the electronic spectra of the azines.

Compound	Band characteristics	B_a and B_b bands (Refs. 68, 72)		Rydberg series, vapour Ref. 68	L_a bands (Refs. 68, 172)			L_b bands for solutions in (Refs. 68,101,127,138,172)					Solutions and vapour (Refs. 107, 127, 134, 138, 174)				
								solvents:									
		vapour	calc.		vapour	calc.	vapour	C_nH_m	water	alcohol	acid	calc.	aqueous	alcoholic	vapour	C_nH_m	calc.
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
						$\pi-\pi^*$ Transitions									$n-\pi^*$ Transitions		
Pyridine	symmetry and polarisation		$^1B_1, x$ $^1A_1, z$		$^1A_1, z$				$^1B_1, x$						$^1B_2, y$		
	position of 0–0 band, Å	1773	1726 1704	1852	2009	1975	2564					2470			2876	2904	2910
	position of maximum, Å	1716														2703	
	ε_{max}							2520 2090	2530 3000	2530 3600							
	oscillator strength	1.3	1.092 1.132	1.3	0.20	0.045		0.03				0.043				0.03	
Pyrimidine	symmetry and polarisation		$^1A_1, z$ $^1B_1, x$		$^1A_1, z$				$^1B_1, x$								
	position of 0–0 band, Å	1705	1732 1667	1777	1911	1920	2481					2435			$^1B_2, y$ 3218	3246	3064
	position of maximum, Å	1666													2960	2985	
	ε_{max}							2430 2030	2430 3210	2430 2920	2420 5540		2710 422	2800 373		326	
	oscillator strength	1.0	1.061 1.125	(0.25)	0.16	0.001	0.044					0.052				0.0069	0.0072
Pyridazine	symmetry and polarisation		$^1B_1, x$ $^1A_1, z$		$^1B_1, x$				$^1A_1, z$						$^1B_2, y$		
	position of 0–0 band, Å	1745	1745 1697		(2000)	1980	2532					2460			3752	(3732)	3831
	position of maximum, Å	1695						2460 1300	2470 1090	2460 1160	2380 1610		3000 320	3110 303	3251	3400 315	
	ε_{max}																
	oscillator strength	(1.0)	1.092 1.117		1.10	0.34	0.020					0.024				0.0058	0.0083
Pyrazine	symmetry and polarisation		$^1B_{3u}, x$ $^1B_{2u}, y$			$^1B_{2u}, y$			$^1B_{3u}, x$						$^1B_{1u}, z$		
	position of 0–0 band, Å	1646 1620	1644 1614	1813	1966	1955	2580 2580				2500				3239	3278	3150
	position of maximum, Å							2600	2610	2610	2820		3049	3100	3239	3278	
	ε_{max}							5600	5800	6000			850	860			
	oscillator strength	1.0	0.987 0.972	(0.25)	0.145	0.134	0.1					0.139				0.010	0.011
1,3,5-Triazine	symmetry and polarisation		$^1E', x, y$		$^1A_1'$				$^1A_2'$						$^1A_2'', z$		
	position of 0–0 band, Å		1625			1808						2265			3167	3192	3141
	position of maximum, Å							2220	2210	2210			2600	2670		2719	
	ε_{max}							146	183	213			747	768		881	
	oscillator strength		1.07			0						0				0.018	0.014
1,2,4,5-Tetrazine	symmetry and polarisation		$^1B_{2u}, y$ $^1B_{3u}, x$			$^1B_{2u}, y$			$^1B_{3u}, x$						$^1B_{1u}, z$		
	position of 0–0 band, Å		1739 1585			1907						2551			5514	5593	4770
	position of maximum, Å							2520	2530				5102		5514	5387	
	ε_{max}							2150	2840				362			829	
	oscillator strength		1.012 1.179									0.123				0.0042	0.011

The rotational structure has been investigated[107], together with the vibrational structure, of the bands of all three diazines. It is important to note that the 0–0 bands proved to be polarised at right angles to the plane of the azine molecule. Apart from the above bands, a study has been made[108] of weak absorption by pyrazine in the region of 3700 Å.

Studies have been made of absorption at shorter wavelengths of 2000–1500 Å by pyrimidine and pyrazine[96] and by all three diazines[68]. The spectra of pyrimidine, pyridazine, and pyrazine have been found to contain respectively four, two, and three bands—at wavelengths of 1932, 1911, 1777, and 1705; 1940 and 1745; and 1960, 1800, and 1650 Å—while a further band at 2000 Å has been suggested in the case of pyridazine. The absorption spectra of the completely deuteriated diazines have also been investigated[68].

(*b*) Spectra of solutions. Absorption spectra in various polar solvents and in hydrocarbons have been obtained for pyrimidine[103,109], pyridazine[110–112], pyrazine[104], and all three diazines[113,114]. This work relates to the sharp bands in the spectra of the vapours, and the following generalisations can be made. Increase in the concentration of a hydroxylated solvent mixed with a hydrocarbon is accompanied by displacement to shorter wavelengths with the intensity practically unchanged, while the vibrational structure becomes diffuse and the absorption continuous. As the acid concentration increases the absorption of all the diazines gradually disappears.

The bands corresponding to the diffuse bands of the vapours exhibit different properties in solvents: a slight hyperchromic effect is observed, while the positions of the maxima remain practically unchanged (in water and hydroxylated solvents). In acidic solvents there is a strong

hyperchromic effect, a bathochromic effect in the case of pyrazine and a hypsochromic effect with the other diazines. A two-step pH variation in ϵ_{max} has been found[115-117] (for all the diazines).

(*c*) Absorption and phosphorescence at low temperatures. The luminescence of pyrazine was first observed[58] in EPA mixture† at 77°K and the corresponding absorption in isopentane at 293°K in the region of 26 000 cm^{-1} with the one progression $\Delta\nu = 606$ cm^{-1}. A more detailed study of the phosphorescence of pyrazine has been made[59] at 90°K in many solvents. From their effect on the spectrum these can be divided into two groups: in EPA, ethanol, and petroleum ether the bands are diffuse in character, whereas in crystalline matrices of carbon tetrachloride, cyclohexane, dioxan, and benzene the bands possess a sharply defined line structure. Analogous investigations have been made[54] on pyrimidine. Other studies have been made[118,119] of the phosphorescence of pyrazine and pyrimidine. An investigation of the phosphorescence of all three diazines showed[120] that pyridazine does not phosphoresce at all.

Polarisation measurements made by the photoselection method[121] have established[122-124] that the phosphorescence of pyrimidine and pyrazine is polarised along the x and y axes respectively (Table 2).

It has been found[125,126] that transitions forbidden by the selection rules are intensified in the absorption of all three diazines in crystals of hydrogen, neon, argon, krypton, and xenon at 4.2°K.

3. 1,3,5-Triazine

Two band systems—sharp and diffuse, with maxima at 36 780 and 45 000 cm^{-1}—have been observed[127] in the absorption spectrum of 1,3,5-triazine vapour. Dissolution in acetonitrile, methanol, and water displaces the maximum of the first band by 520, 670, and 1670 cm^{-1} respectively to shorter wavelengths compared with the solution in cyclohexane, while the maximum of the second band does not move. The vibrational structure of the first band has been analysed[128]. It was established from the rotational structure that the permitted electronic transition corresponds to polarisation perpendicular to the plane of the molecule. Besides absorption, phosphorescence has been observed[129] in EPA solution at 77°K, as a band with its origin at 26 400 cm^{-1}. This work also revealed absorption in the range 13 000–31 000 cm^{-1}, which had not been noted in the earlier work[127].

4. 1,2,4,5-Tetrazine

Symmetrical tetrazine is characterised by absorption in the visible region with a pink colour[130-133]. A detailed investigation of the absorption spectrum over a wide range, 15 000–45 000 cm^{-1} (6000–2200 Å), has shown[134] the presence of strong absorption with a maximum at 2520 Å and a shoulder at 3200 Å, together with a sharp band system in the region of 18 000 cm^{-1}. In aqueous solution the shoulder and the visible absorption are displaced to shorter wavelengths. Studies have been made[76,77] of the vibrational structure at high resolution in the visible absorption of symmetrical tetrazine and its deuterium analogue (in the vapour state and in solutions). An important result of the rotational analysis[135] of the 0–0 band at 5515 Å was the finding that the molecule has a planar structure in the excited electronic state and that polarisation of the electronic transition is perpendicular to the plane of the molecule. Examination of the fluorescence in various solvents at 77°K and comparison with the absorption spectrum showed a mirror-image relationship between the emission and absorption spectra[136,137]. The vibrational structure becomes blurred on passing to solvents in which hydrogen bonding occurs, and the fluorescence undergoes an anomalous shift to longer wavelengths, in contrast to the opposite shift in the absorption.

Combined data will be found[114,138] on frequencies and wavelengths of the 0–0 bands, the band maxima, oscillator strengths, and molar absorption coefficients in the spectra of all azines and many of their derivatives in various solvents. All the most important experimental spectral data for the azines are given in Table 4.

B. THEORETICAL WORK ON ABSORPTION AND EMISSION SPECTRA

1. Comparative Characteristics of $\pi-\pi^*$ and $n-\pi^*$ Transitions

The old problem of the interrelationship between the absorption spectra of molecules and their structure is soluble in principle by quantum mechanics. The subdivision of electrons in a molecule into σ- and π-electrons has enabled regions corresponding to optical transitions of these electrons ($\sigma-\sigma^*$ and $\pi-\pi^*$ transitions, both denoted $N\rightarrow V$) to be delineated in the absorption spectra of hydrocarbons. In the case of aromatic systems containing heteroatoms, transitions of the lone-pair electrons to vacant σ^*- and π^*-orbitals ($n-\sigma^*$ and $n-\pi^*$ transitions, both denoted $N\rightarrow Q$) must also be taken into account. Since transitions of types $\pi-\pi^*$ and $n-\pi^*$ correspond to the same spectral region, the problem arises of establishing criteria by which they can be distinguished. The comparative characteristics of transitions of the two types are listed in Table 5, which is based on Refs. 139–142 and an analysis of experimental results. We will briefly clarify the main generalisations in this table.

Since an $n-\pi^*$ transition involves passage of the electron from a non-bonding orbital to an antibonding π^*-orbital, and a $\pi-\pi^*$ transition occurs from a bonding orbital to the same antibonding orbital, the former transitions will correspond to longer wavelengths. The low intensities of $n-\pi^*$ transitions are explained by the fact that only the $2s$-function of the hybrid orbital of the n-electron, which weakly overlaps the p-function of the upper state, makes a contribution to the transition dipole moment[140]. The polarisation properties are determined by the symmetry of the orbitals in the lower states of transitions of both types: n-orbitals are symmetric, while π-orbitals are antisymmetric, with respect to the plane of the molecule.

In a hydroxylated solvent conditions are created for the formation of hydrogen bonds of the type N...H–O, which stabilise the lone pair of electrons and therefore produce a

† A solvent comprising 5 parts of diethyl ether, 5 parts of isopentane, and 2 parts of ethanol by volume—cf. G.H.Lewis and D.Lipkin, J. Amer. Chem. Soc., 64, 2801 (1942) (Ed. of Translation).

TABLE 5. Comparison of chief characteristics of $n-\pi^*$ and $\pi-\pi^*$ transitions in the spectra of azines.

Band characteristics	$n-\pi^*$ Transitions	$\pi-\pi^*$ Transitions
Wavelength (for the first transitions)	2700–5500 Å	2500 Å
Molar extinction coefficient	300–1000	1000–6000 (except for 1,3,5-triazine)
Polarisation of absorption for singlet–singlet transitions	Allowed transitions polarised perpendicular to the plane of the molecule	Allowed transitions polarised in the plane of the molecule
Effect of a polar solvent (compared with the spectrum in a hydrocarbon) (*a*) alcohols and water	Hypsochromic shifts without substantial change in intensities; position of maximum depends on concentration of hydroxyl-containing solvent	Effect insignificant
(*b*) acid	Gradual weakening of absorption, until it disappears as the acid concentration increases	Always a hyperchromic effect, the intensity depending on the acid concentration; the magnitude and direction of the shift depend on the compound
Vibrational structure	Very sharp in vapour and crystals, less sharp in hydrocarbon, and becomes indiscernible in polar solvents	Diffuse
Vibrational progressions	The main frequencies forming progressions are those of totally symmetric deformation vibrations of the ring	Frequencies of totally symmetric stretching vibrations are involved
Envelopes of electronic–vibrational bands	They possess atomic sharpness; rotational structure resolved	Diffuse
Shift on conjugating substitution	Hypsochromic	Bathochromic

hypsochromic effect. This view is supported by measurements [112,143] indicating that the energy represented by the displacement of the absorption band for pyridazine and the energy of the hydrogen bond are equal. The band maximum shifts with increasing concentration of the solvent, and this has been used to investigate complex formation. Hydrogen bonding is concerned in the explanation of the hypsochromic shift based on the Franck–Condon principle [118,119].

In acid solution protonation occurs, accompanied by a strong hypsochromic shift in the $n-\pi^*$ transition. With increasing acid concentration, therefore, the gradual "disappearance" of the band is observed in the region examined. Calculation shows [144,145] that protonation changes the field of the skeleton and increases the oscillator strength of $\pi-\pi^*$ transitions, whereas the direction of displacement of the band depends on the nature of the solute and differs for the various azines. Hydrogen bonding or protonation leads to a broadening of the vibrational bands and a diffuse character of the vibrational structure of the transition.

Doubt has been cast [146] on the method of differentiating between $n-\pi^*$ and $\pi-\pi^*$ transitions based on the comparative characteristics described above. It is stated that the observed changes in the spectra produced by a solvent can be explained not only by local interactions between the two molecules but also by the general influence of the internal field in a liquid. A rather more conclusive method is therefore proposed for detecting $n-\pi^*$ transitions, based on hydrogen-bond formation in a non-polar solvent. For this purpose a small amount (0.01 M) of a feebly dissociated acid is added to a solution of the azine in a hydrocarbon. The $n-\pi^*$ transitions in the spectra of azines dissolved in hexane were investigated [146] in the presence of acetic acid, methanol, and phenol. A solution containing no proton-donor was taken as zero for the readings. An advantage of the method is that the concentration of the chromophore is not limited, and the investigation is made in the range of validity of the Lambert–Beer law.

After the bands observed experimentally in the spectra of azines have been assigned, the problem arises of a quantitative theoretical determination of the frequencies and intensities of transitions, with their classification on the basis of the symmetry properties of the molecules. This problem is solved by the three main methods of quantum chemistry—valence pairs, molecular orbital, and free electron methods—using group theory.

2. Calculation of Excited Electronic States and Main Parameters of Electronic Transitions

(*a*) $\pi-\pi^*$ Transitions. Present-day calculations can be subdivided into simplified calculations, in which the transition energy is determined as the energy of excitation of one electron, and more exact calculations, in which the wave function of a molecule is built up as an antisymmetrised product of molecular-orbital and spin functions, the interaction of the electrons and their configurations being taken into account.

The first type includes calculations by the sample Hückel method, which have been made for pyridine [95,147] and for all the azines [148,149]. In the last of these [149] second-order perturbation theory was included within the framework of the simple molecular-orbital method. The calculation has been made also for symmetrical tetrazine [150]. All such calculations are semi-empirical in character, and enable only the position of the absorption band of longest wavelength to be predicted. Only one paper [149] has compared the positions of such bands in a series of azines. Another variant of the same one-electron approximation is the free-electron model, in which the role of the heteroatom is allowed for by introducing an additional potential well near it. A particularly large number of such calculations have been made for pyridine [151–155]. The last of these papers includes a calculation of the energy of the first transition in pyrimidine. In another case [156] σ-potentials were introduced for the nitrogen atom in pyridine, pyrazine, and 1,3,5-triazine. A somewhat modified form of the method has been applied to pyridine and pyrazine [157]. The possibilities of all such calculations are confined to computation of the wavelength of the first band, while greater errors are involved in determination of oscillator strengths, and singlet and triplet states are not distinguished with respect to energy.

A far more complete description of the spectra is obtained by more exact methods. In the first, widely known attempt of this type [158] the various integrals were estimated by a semi-empirical method, and calculations made of the positions of singlet and triplet levels, oscillator strengths, and also bond orders in pyridine, pyrimidine, pyrazine, and 1,3,5-triazine. A detailed analysis has been made [159] of Pariser and Parr's method [158]. An analogous calculation for 1,2,4,5-tetrazine allowed for configuration interaction [160,161]. These last calculations, however, gave an unsatisfactory result owing to an unfortunate choice of orbitals for the initial approximation, although the resonance integral of the nitrogen–nitrogen bond calculated in this work (−2.35 eV) became generally accepted.

At a further stage calculations were made by the self-consistent field (Pariser–Parr–Pople) method[162], using the Pople approximation[163] for the Hartree–Fock Hamiltonian, together with a semi-empirical estimate of various integrals[158]. These calculations were made[164-166] with the separation of a term common to all the azines, and representing the electron affinity of the nitrogen atom, in the coulombic integral at the atom. With a single choice for this parameter it was possible to predict satisfactorily four excited singlet states for all the azines other than symmetrical tetrazine. The best results in calculating the energies of excited states are achieved[167] by using self-consistent orbitals including a limited number of configuration interactions. Calculations of the same type, but with a somewhat different estimate of the electronic interaction integrals, were made for pyridine, pyrazine, and 1,3,5-triazine[168,169] and for 1,2,4,5-tetrazine[170]. The same method has been used[171] in calculations for all the azines other than symmetrical tetrazine. However, agreement with experimental values for the transition frequencies proved unsatisfactory. The best results for all the azines (singlet and triplet states, oscillator strengths) were obtained[172] by taking into account the dependence of the resonance integrals on the bond lengths in the series of azines (these results are given in Table 4).

Analysis of all the calculations listed above leads to the conclusions that the electronic configurations between which significant interaction occurs are of the same type in benzene and in the azines. A parallel classification of electronic transitions in the spectra of these molecules is therefore possible.

Calculation by the self-consistent field method, with interaction of the electrons taken into account, does not ensure a sufficiently exact description of excited states. Such a description is considerably improved by allowing for configuration interactions, the most important of which are those corresponding to transitions from two filled upper orbitals to two vacant lower orbitals. A good interpretation of the electronic spectra is then achieved.

With regard to the vibrational structure of $\pi-\pi^*$ transitions, the angles retain their equilibrium values on excitation of a π-electron, while the bonds become only slightly longer. In conformity with the Franck–Condon principle, therefore, the frequencies of totally symmetric stretching vibrations in the excited state should be the most intense[173]. Experiment confirms this conclusion: progressions with the frequencies of totally symmetric stretching vibrations are observed in the absorption spectra of pyridine[93] and the diazines[68,106] in the region of 1550–2000 and 2500 Å.[68]

(*b*) $n-\pi^*$ Transitions. A more fundamental rearrangement of the whole electron shell of the molecule is produced by this transition. The nitrogen atom acquires a positive charge, while a seventh electron appears in the π-electron system. In the excited state, therefore, the properties of the hybridised functions[174] of the nitrogen atom are changed, while the change in the skeleton affects also the π^*-electron functions. These changes complicate the calculations, which are less satisfactory in the case of $n-\pi^*$ transitions.

A simplified model, in which the interaction between a pentadienyl radical and a nitrogen atom having two *p*-electrons is considered, has been used[175] to calculate the energy of the first $n-\pi^*$ transition in pyridine. Since delocalisation of the seventh electron was ignored, the calculation proved unsatisfactory.

An extended form of the Pariser–Parr method, in which the n-electrons were explicitly allowed for in calculating the atomic integrals, was used in a series of papers[176-179]. The energies of the singlet and triplet states of pyrimidine and pyrazine were calculated. However, a satisfactory result was obtained only on the assumption that the 2*s*-function participated to a small extent in hybridisation, in both ground and excited states. But this hypothesis leads to difficulties in explaining the valency angles in the ground state and the intensities of the transitions[174]. The hybridisation parameter was not calculated theoretically, but merely estimated from spectroscopic data.

This defect is absent in calculations[180], without variation of the hybridisation parameter, of the singlet and singlet–triplet transition energies in pyridine, pyridazine, and pyrimidine. The energy of the ground state was determined as the sum of the energies of six π-electrons in the field of the nuclei and the energy of one electron in a doubly occupied orbital, whereas the energy of the excited state was regarded as the energy of seven electrons in the field of the skeleton with a double positive charge on the nitrogen atom. Various integrals on which the difference between these energies depends were computed[180]. But the calculation made it possible to find only mean values of singlet and triplet states. These states could then be separated by application of a method[181] taking into account exchange interactions.

Nevertheless, the most complete description of the spectra of all the azines was accomplished by means of semi-empirical calculations to the one-electron approximation[114,174,182]. These papers showed that the energy of $n-\pi^*$ transitions was determined by two factors—the fall in the energy of the molecular orbitals of the π^*-electrons on introduction of the heteroatom, and the interaction between n-electrons in different atoms—the first factor being due to the enhanced electronegativity of the nitrogen atom relative to carbon, and the second being most significant in the presence of adjacent nitrogen atoms. When these factors were taken into account, the shifts in the $n-\pi$ bands relative to pyridine could be explained throughout the series of azines.

1,3,5-Triazine is especially interesting, since in this molecule the highest filled n-orbitals and the lowest vacant π^*-orbitals are degenerate. Allowance for the configurational interaction eliminates this degeneracy. Calculation of the removal of degeneracy revealed[183] that the resolution is small (around 1 eV) with various sets of semi-empirical values for the integrals, while all transitions between sublevels lie within the same band at 3200 Å.

The oscillator strengths f vary in the series of azines (see Table 4). These changes have been explained[174] by changes in the degree of delocalisation of the π-orbitals and differences in configuration interactions, which play an important part in the calculation of f. Accompanying calculations[174] of differences in energy between singlet and triplet states yielded reasonable values only on the assumption of a small participation of 2*s*-functions in the hybrid functions of the excited states. The above calculations determine the positions of excited singlet and triplet energy levels in azines, which are required in order to explain both absorption and emission spectra. However, the latter exhibit specific regularities. Among all the azines[137] only 1,2,4,5-tetrazine fluoresces, whereas pyrimidine and pyrazine exhibit intense phosphorescence. Pyridine and pyridazine do not luminesce at all. The reasons for these phenomena have been cleared up[184]. The lowest excited

singlet state in azines is an $S(n,\pi^*)$ state. The probability of a transition from it to the ground state is very small. But this is not the main reason for the absence of fluorescence. The main competing process suppressing it is a radiationless transition from the $S(n,\pi^*)$ state to a triplet state $T(\pi,\pi^*)$, located below the former state. This follows from a calculation of the probability of such a transition, which becomes possible as a result of spin–orbital interaction. Such a transition does not occur in symmetrical tetrazine, since the $T(\pi,\pi^*)$ level is located above the $S(n,\pi)$ level, and this compound therefore fluoresces. Phosphorescence is due to an intersystem transition from the $T(n,\pi^*)$ state to the ground state. Such a transition, however, may be radiationless. It is supposed [184] that in pyridine and pyridazine the probability of this process is high. But this explanation does not settle the problem, since this probability has not been determined, and the reason for the phosphorescence of pyrimidine and pyrazine remains obscure.

C. PRINCIPLES OF THE CLASSIFICATION OF ELECTRONIC STATES AND THE INTERPRETATION OF ELECTRONIC SPECTRA

Group theory provides the most general method for classifying electronic energy levels. The symmetry type of each electronic configuration is determined as the direct product of the symmetry types of molecular orbitals filled with one or two electrons. The ground state of the molecule is totally symmetric. When configuration interaction is taken into account, two cases must be distinguished: if the interacting configurations are not degenerate, the resultant state possesses the symmetry of the individual configuration (only configurations of the same symmetry type interact); if, however, one or more interacting configurations are degenerate, several states of different symmetry types arise. The notation for the excited states and transitions is identical with that of the symmetry types.

The second method is applied especially to cyclic systems containing conjugated bonds [185]: the one-electron energy levels are classified according to the values of the projection m_q of the angular momentum on an axis perpendicular to the plane of the molecule. If the sum of the m_q over all electrons in the molecule is 0, ±1, ±2, ±3, the states are denoted for monocyclic systems by A, B, C, L. A state having $\Sigma m_q \neq 0$ is doubly degenerate. The presence of a heteroatom eliminates the degeneracy, and the components of the splitting are denoted by Ba, Bb, Ca, Cb, La, Lb. A one-to-one correspondence is stated [186] to exist between the notations of the two methods, which are indicated in Table 4. Finally, the purely empirical notation—α, p, β, β'—was introduced [187] for transitions from the ground state to the states ^1L_b, ^1L_a, ^1B_b, and ^1B_a. The applicability of this notation to azines has been justified [164,167] by comparing the energy levels and the spectra of the azines and benzene. All these symbols are applicable only to $\pi-\pi^*$ transitions. Only the symbols of group theory are to be used for $n-\pi^*$ transitions, since the properties of n-electrons are not in general represented by the model of free electrons on which the notation of Ref. 185 was based.

The symbols of the transitions are closely linked with their polarisation properties. For singlet–singlet transitions the polarisation is unambiguously defined by the symbol of the upper state and the symmetry types of Cartesian coordinates. To establish the polarisation of a singlet–triplet transition it is necessary to know the symmetry of the sublevels into which the triplet level splits as a result of spin–orbit interaction. Such determinations have been made for the azines [188].

Interpretation of Electronic Spectra

Analysis of the above experimental and theoretical work enables a complete interpretation to be given for the absorption and luminescence spectra of the azines. The absorption spectra are set out in Table 4, in which columns 3–13 give the main characteristics of the $\pi-\pi^*$ transitions, and columns 14–18 those of the $n-\pi^*$ transitions. Assignment of the former transitions was based on the correspondence between the spectra of the azines and that of benzene. Theory predicts for pyridine and the diazines two transitions each in the range 1600–1700 Å. Only one maximum is observed experimentally in this range, which is consistent with the small degree of resolution of the benzene band at 1790 Å. The La-bands correspond to the benzene band at 2050 Å. They show a marked discrepancy between calculated and measured oscillator strengths, which may be tentatively explained by superimposition of a $\sigma-\pi^*$ transition in the same region. The Lb-bands correspond to the benzene band at 2600 Å, and are less intense than the B-bands.

As early as 1954 [127] all the long-wavelength sharp band systems were assigned to $n-\pi^*$ transitions on the basis of a study of solvent effects. Analysis of the rotational structure of corresponding 0–0 bands of diazines [107], 1,3,5-triazine [128], and 1,2,4,5-tetrazine [135] showed them to be polarised perpendicularly to the plane of the molecule. This fact finally confirms the assignment of the transitions to the $n-\pi^*$ type. Table 4 shows very clearly the effects of solvents on transitions of both types.

It follows from the scheme of energy levels [174] that a second permitted $n-\pi^*$ transition occurs in pyrimidine, pyridazine, and symmetrical tetrazine. To such transitions have been assigned the bands at 1932 and 1942 Å in pyrimidine and pyridazine [68] and at 3200 Å in 1,2,4,5-tetrazine [134]. The positions of the bands agree with theoretical predictions [174], but their assignment is tentative, and they are not included in Table 4.

While Table 4 indicates only singlet–singlet transitions, the singlet–triplet transitions are given in Table 6. [174] The latter are assigned to intersystem transitions in view of the long life-time of the excited states and the small oscillator strengths [174,188]. The important part played by radiationless transitions from excited states of the molecules was already pointed out in the early work [139,140]. In most cases, therefore, the nature of the radiating transition ($\pi-\pi^*$ or $n-\pi^*$) is determined by the type of the lower excited state, and the type of phosphorescence depends on the relative positions of the $T(\pi,\pi^*)$ and $T(n,\pi^*)$ levels [189]. Theoretical calculation is not a reliable criterion, since these states may be very close together, and the distinguishing features listed in Table 5 are used to assign the $S-T$ transitions.

The symmetry types indicated in Table 6 have been established from the correspondence with absorption bands and the law of mirror symmetry. Symmetrical triazine forms an exception. The long life-time indicates that the transition is forbidden not only with respect to spin but also with respect to symmetry. The transition is therefore assigned not to $^3A_2''$ but tentatively [174] to $^3E''$. Table 6

TABLE 6. Intersystem transitions in azines.

Compound	Position of 0–0 band, Å		Life, s	Assignment and polarisation
	absorption	phosphorescence		
Pyridine	3381	—	—	$^3A_1(\pi, \pi^*)$
Pyrimidine	—	3534		$^3B_2(n, \pi^*)$, x
Pyrazine	3765	3769	$2\cdot10^{-3}$	$^3B_{1u}(n, \pi^*)$, y
1,3,5-Triazine	(3846)	(3788)	0.46	$^3E''(n, \pi^*)$

does not include the luminescence of symmetrical tetrazine, since the band at 5571 Å is assigned, in view of the short life-time and on the basis of the law of mirror symmetry, to the singlet–singlet transition $^1B_{1u}$: i.e. it is fluorescent.

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GAS CHROMATOGRAPHY WITH TEMPERATURE PROGRAMMING

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1. INTRODUCTION

The gas-chromatographic analysis of complicated mixtures of organic compounds, differing markedly in partition coefficients, almost always requires the application of a variable temperature. In fact, it is impossible to choose a constant temperature such that light and heavy components can be separated satisfactorily in the same analysis. If a low temperature is chosen, light components will be separated satisfactorily, but a long time will be required to analyse the heavy components. Furthermore, because of the considerable spreading of the peaks, the sensitivity of the chromatograph will be too low for the heavy components. At a high temperature the heavy components readily show up, but the retention time of the light components is so short that they cannot be separated even on a highly efficient column.

The problem has been solved by applying to the mixture to be separated either a moving temperature profile with a constant temperature gradient in the direction of flow of the carrier gas, or by varying the temperature simultaneously along the whole column.

The former method was proposed and developed by Zhukhovitskii and Turkel'taub together with their collaborators [1-5], and is termed stationary chromathermography. In this method the components of the mixture are distributed inside the column in such a way that the less volatile substances are located near the inlet, where the temperature is higher, and the more volatile substances near the outlet. The components remain practically stationary relative to the furnace producing the temperature gradient, and move towards the outlet from the column at the same speed as the furnace gradient. In the course of time the bands shrink and the mixture becomes enriched.

The other method, which has been called the programmed temperature method, was proposed by Griffiths et al. [6] Temperature programming permits the light components to escape at low temperatures, and the heavy components at high temperatures. In this way an acceptable retention time is obtained, together with quite narrow peaks for both light and heavy components.

At the present time the temperature programming method, which is simpler in practice, is predominantly used, and most of the papers have been devoted to it. Undoubtedly the stationary chromathermography method also shows promise, and will be developed in the future. The present paper discusses only the temperature programming method. A detailed description of stationary chromathermography can be found in two monographs [7,8].

The practice of temperature programming has developed greatly. A theory has been constructed which enables results for isothermal chromatography to be used to determine the retention temperature, ascertain the degree of component separation as a function of the operating conditions, and identify the components of a complex mixture.