thermodynamic stability of the silicides and the high affinity of the components for oxygen reveals a possible application for deoxidising in metallurgy and as special hardeners for introducing the rare-earth metals into various types of glass. Individual silicides are probably of interest as scale-resistant components in alloys with high-temperature strength.

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THE MOLECULAR STRUCTURE OF 1,3,5-TRIAZINE AND ITS DERIVATIVES

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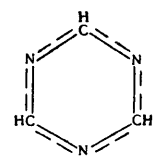
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1. INTRODUCTION

One of the sensational scientific achievements of recent years has been the long awaited discovery of free symmetrical triazine. It has turned out that this compound was first obtained by Nef[1] as early as 1895, but owing to errors in determining its molecular weight, he ascribed to this substance an incorrect structural formula, regarding it as a dimer of hydrocyanic acid. This view was shared by other investigators for more than half a century (see, for example, Hinkel and Summers[2]).

It was only in 1953 that Grundmann and Kreutzberger[3] again determined the molecular weight of the product described by Nef, and found, to their surprise, that it was a trimer of hydrocyanic acid, its molecular structure being that of symmetrical triazine (I):



(I)

Intensive research on the physicochemical properties of 1,3,5-triazine gave an immense amount of information, not yet fully systematised, which enables a fairly complete picture to be obtained of its molecular structure, which is of considerable theoretical importance.

Many derivatives of 1,3,5-triazine are of no less theoretical and practical interest. Thus melamine (2,4,6-triamino-1,3,5-triazine), cyanuric acid (2,4,6-trihydroxy--1,3,5-triazine), cyanuric chloride (2,4,6-trichloro-1,3,5--triazine), and several others have become of definite and

TABLE 1. Additional conventional notation for fractional bond orders (examples).

Type of bond	Bond order: graphical symbol	Bond order: numerical symbol
Weak bond	·····	$n=\frac{1}{\infty}$
Weaker than single	⌒	$n<1$
Single	—	$n=1$
Stronger than single	·····	$n>1$
Bond order 1⅓	═	$n=1^1/_3$
Weaker than 1⅓	≈	$n<1^1/_3$
Stronger than 1⅓	≋	$n>1^1/_3$
"Sesqui-bond" (1½)	═	$n=1^1/_2$
Weaker than 1½	≈	$n<1^1/_2$
Stronger than 1½	≋	$n>1^1/_2$
Double bond	═	$n=2$
Weaker than double	⌒	$n<2$
Stronger than double	⌓	$n>2$
Triple bond	≡	$n=3$
Weaker than triple	≡	$n<3$

continually increasing importance in the plastics, paper, paint, pharmaceutical, and several other industries. These compounds, discovered in the dawn of organic chemistry (melamine was discovered by Liebig[4] in 1831, cyanuric acid[5] in 1828), are now produced in quantities of many tons. The chemical properties of 1,3,5-triazine derivatives and associated technological problems are discussed in detail in several monographs and reviews[6,7].

The peculiar molecular structure of these substances makes them also of great theoretical interest. This aspect is hardly considered in the reviews which have been cited.

The present review discusses the molecular structure of 1,3,5-triazine and its derivatives in the light of work on the determination of interatomic distances and the investigation of vibrational and electronic spectra.

Since almost all the compounds under consideration contain fractional chemical bonds, the classical method of graphical representation of molecular structure is not always adequate. We shall therefore use a system of extra conventional symbols suggested by one of us[8]. This system is based on two principles: (1) division of the line representing the bond into a number of parts equal to the denominator of the fractional part of the bond multiplicity; and (2) the use of arcs to denote weakening or strengthening of the bond (in the former case the arc is convex towards the line denoting a σ-bond, while in the latter case it is convex in the opposite sense).

The most frequent cases of fractional bond multiplicity and their symbols are shown in Table 1. Plus and minus signs are used, as is customary, to denote partial positive and negative charges, and also a partial radical state. Weak partial charges are placed in circles, stronger partial charges in parentheses.

A detailed description and examples of the use of this additional conventional notation have been published previously[8]. The present review gives further examples of the usefulness of introducing a definite system of additional symbols, enabling a single structural formula to represent the detailed structure of molecules containing conjugated bonds (both with $\pi-\pi$ and with $n-\pi$ conjugation).

2. INTERATOMIC DISTANCES AND BOND MULTIPLICITY

Up to the present time, very few data have become available on interatomic distances in 1,3,5-triazine and its derivatives. Results obtained by individual investigators often vary among themselves by an amount exceeding the experimental error. In several cases data on interatomic distances are inconsistent with general theoretical ideas. Fresh, more reliable and more exact data are required.

Table 2 summarises published information on interatomic distances in these compounds. The most reliable and unambiguous values are those for melamine, cyanuric chloride, and cyanuric acid; the remaining data require critical examination.

The C–N interatomic distance in free 1,3,5-triazine (I) is of great theoretical significance, being the only example of the "sesqui-bond" [bond order 1.5 (Ed. of Translation)] $C_{sp^2}-N_{ps}$. Therefore the discrepancy in the experimental results[9,10], making it necessary to choose the "best" value on the basis of other considerations, is very unfortunate. Since the C–N distances in 1,3,5-triazine cannot be greater than the length of the corresponding bond in cyanuric chloride (II) and should be considerably less than the $C-N_r$ distance in melamine†, the results of Wheatley's X-ray measurements[9] must be accepted as the more likely to be correct. The mean length of the C–N "sesqui-bond" has been taken[17] as 1.325 Å.

The C–Cl distance in cyanuric chloride is almost equal to that in chlorobenzene[18] (1.69 ± 0.03). The decrease in the C–Cl distance compared with its value in alkyl chlorides[19] is considerably greater than the decrease due to the change in valency state of the carbon atom, which in this case (transition from sp^3 to sp^2 state) is estimated[20] at about 0.02 Å. The remainder of the decrease in interatomic distance must be ascribed to the interaction of the 1,3,5-triazine ring with the chlorine atom, as shown in the structural formula (II).

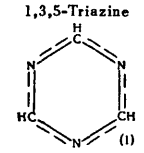
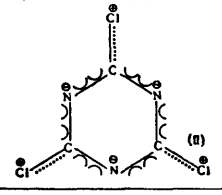
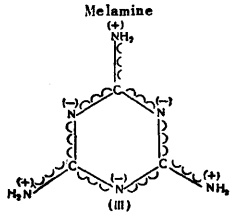
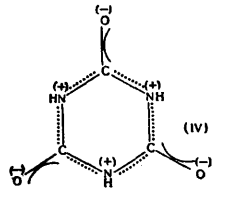
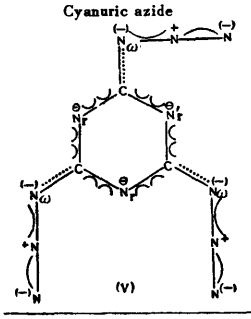
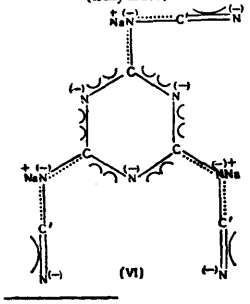
The length of the C–N bond in cyanuric chloride is very close to 1.5. The order‡ of this bond[17] is close to 1.43. On the hypothesis that the sum of the multiplicities of the bonds associated with a carbon atom is 4,[17,21] we can estimate the multiplicity of the C–Cl bonds in cyanuric chloride as close to 1.15.

Some explanations require that positive charges shall be written on the chlorine atoms. The physical significance of these symbols is that they indicate a decrease in the negative charge on the chlorine atom resulting from the electrical dissymmetry of the C–Cl bond caused by interaction of the ring π electrons with lone electron pairs on the chlorine atom.

† Here and subsequently, the subscript "r" indicates a cyclic nitrogen atom, and "ω" a nitrogen atom outside the ring.

‡ The term "bond order", or more precisely "bond multiplicity", will be applied to the number of pairs of electrons associated with a given bond[20].

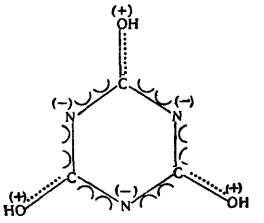
TABLE 2.

Compound	Bond length, r, Å	Bond order, n	Method of determination	Ref.
1,3,5-Triazine  (I)	$C-N_r$ 1.319±0.005 C—H 1.00	1.5	X-ray	9
	$C-N_r$ 1.338±0.001		rotational structure of Raman spectrum	10
Cyanuric chloride (2,4,6-trichloro-1,3,5-triazine)  (II)	$C-N_r$ 1.33±0.02	1.43	electron diffraction	11
Melamine  (III)	$C-N_r$, 1.33±0.01	1.35	ditto	11
	$C-N_\omega$ 1.37±0.03	1.25		
	$C-N_r$ 1.33—1.35	1.35	X-ray	22
	$C-N_\omega$ 1.35—1.36	1.30		
	N—H...N 3.00—3.10			
Cyanuric acid  (IV)	$C-N_r$ 1.36±0.06	1.23±0.15	ditto	15
	C—O 1.28±0.06	1.42±0.22		
	N—H....O 2.80			
	$C-N_r$ 1.36±0.02	1.29±0.07	»	13
	C—O 1.28±0.03	1.42±0.15		
	N—H....O 2.80			
Cyanuric azide  (V)	$C-N_\omega$ 1.38	1.22	»	14
	$C-N_r$ 1.38	1.22		
	$C-N_r$ 1.31	1.53		
	N_ω—N 1.26			
	N—N 1.11			
Sodium tricyanomelaminate (trihydrate)  (VI)	$C-N_r$ 1.34—1.35	1.35—1.30	»	12
	$C-N_\omega$ 1.40	1.15		
	1.32	1.30		
	1.21	2.20		
	(1.34—1.35)*	(1.35—1.30)		
	1.36—1.33	1.30—1.40	calculated[21]	21
	(1.32)	(1.30)		
	1.17	2.70		

* Accepted values are in parentheses.

The interaction between π electrons of the triazine ring and the lone pairs on the nitrogen atoms in the melamine molecule is so strong that it leads to almost complete equalisation of the lengths and multiplicities of the C-N bonds. Only a slight difference in bond lengths, and especially the arrangement of the hydrogen atoms, enable us to assume that, in the crystalline state, melamine is in the amino-form. Published methods[23] for preparing the imino-form ("isomelamine") have been shown[22] to give the same amino-form as do all other methods for preparing melamine.

A notable feature of the structure of cyanuric acid is the absence of conjugated bonds in the 1,3,5-triazine ring and the presence of three carbonyl bonds (oxo-form). It is difficult to decide directly from the interatomic distances to what extent the structure of cyanuric acid is close to the oxo-form or to the hydroxy-form (VII), since in both cases intermediate values are observed for the bond lengths. Determination of bond multiplicities from the hybrid bond length/multiplicity curves shows that the observed interatomic distances correspond to formula (IV), not (VII). Thus the benzenoid structure with $\pi-\pi$ conjugation proved less advantageous than the structure having carbonyl bonds. This is explained[24] by the fact that the carbonyl bond is energetically more favourable than the multiple C–N bonds, while the loss in $\pi-\pi$ conjugation is to a considerable extent balanced by strong $n-\pi$ conjugation.



(VII)

The data on interatomic distances in cyanuric azide (V) probably contain an error: there are absolutely no reasons why the C–N distances in the ring should be different. The mean, 1.34–1.35 Å, of the distances given[14] is most probable, corresponding to a bond multiplicity of 1.35–1.30.

Among the interatomic distances in sodium tricyanomelaminate[12] those of $C-N_\omega$ and C...N (Table 2) are doubtful. Actually, calculation of the sums of the bond multiplicities gives 3.65–3.85 for the ring carbon atoms and 3.50 for the nitrile carbon atoms, instead of the expected 4. If the interatomic distances in the ring are regarded as correct, and the sum of the bond multiplicities given by the carbon atoms is taken as 4, the orders of the C–N and C≅N bonds are easily found to be 1.30–1.40 and 2.70 respectively. Hence from the hybrid bond relationship we obtain interatomic distances of 1.36–1.33 and 1.17 Å.

The general conclusion which follows from the data considered here is that the observed interatomic distances differ markedly from the lengths of "pure" single, double, and triple bonds. The difference can be measured by determining from the curve the multiplicity (order) of the given bond. In several cases it is possible, from the postulate that the aggregate multiplicity of the bonds emanating from a carbon atom is 4, to assess the correctness of the results obtained or to predict interatomic distances which have not yet been measured.

It is curious also that the 1,3,5-triazine ring, like the benzene ring, can act either as a donor or as an acceptor of electrons.

3. VIBRATIONAL SPECTRA

A great deal of information has now accumulated on the infra-red spectra of 1,3,5-triazine and its derivatives. However, owing to the experimental difficulties associated with the absence of suitable solvents and the impossibility of obtaining stable liquids, available data on the Raman spectra are confined to 1,3,5-triazine, cyanuric acid, and cyanuric chloride.

Table 3 shows the vibrational properties of 1,3 5-triazine molecules (symmetry D_{3h}).

Experimental results on the infra-red and Raman spectra of 1,3,5-triazine and its deuterated derivatives are given in several papers [26-28].

The frequencies were assigned on the basis of calculations using Urey–Bradley potential functions [29] and a valence-force model [30] (Table 4), the frequencies being numbered after Herzberg [31].

Two frequencies of class A_2' are forbidden in the spectrum of 1,3,5-triazine, and one E″ frequency is not observed because of its very low intensity; calculated values of these frequencies are given in Table 4. The class A_1' frequencies 1132 and 992 cm^{-1}, class E′ frequencies 1555, 1410, and 675 cm^{-1}, and the A_2'' frequency 735 cm^{-1}, which are characteristic and appear in the spectra of derivatives, are assigned to vibrations of the 1,3,5-triazine ring [28].

Table 5 traces the frequencies of these vibrations in the infra-red spectra of various 1,3,5-triazine derivatives having D_{3h} symmetry.

It is evident from Table 5 that all the characteristic frequencies persist in the spectra of the most varied derivatives. The A_2'' frequency falls roughly in conformity with increase in multiplicity of the C–N bonds in the ring.

Special interest attaches to investigations of the vibrational spectrum of cyanuric acid (IV), which first enabled the prolonged controversy about its molecular structure to be settled. The first investigation of the Raman spectra by Kahovec and Kohlrausch [32] showed that, in the solid state, cyanuric acid exists not in the hydroxy-form (VII), as many had supposed [33], but in the oxo-form (IV). This conclusion was subsequently confirmed by numerous investigations [15,34-38] of the infra-red spectra. The basis for such a conclusion was the intense absorption band with $\nu_{max} \simeq 1710$ cm^{-1}, which is clearly due to the characteristic vibration of the carbonyl group.

It is interesting that the carbonyl frequency in cyanuric acid is appreciably higher than in urea [39] (1686 cm^{-1}), although the interatomic distance and hence the multiplicity of the carbonyl bond are similar in these molecules ($r_{C=O}$ is 1.262 Å in urea [40] and 1.28 Å in cyanuric acid [14]). This may be due [37] to mechanical causes, such as strain in the ring.

An attempt at assigning frequencies in the vibrational spectrum of cyanuric acid was made by Newman and Badger [15], but their investigation cannot be accepted as complete or reliable, since the assignment of several frequencies is open to doubt.

The spectrum of cyanuric acid contains more than one absorption band within the range of N–H vibrations, which is probably consistent with the idea that more than one type of hydrogen bond is present [15,41]. The intensity and position of the NH-frequencies depend on the mode of preparation of the specimen (as a sublimed layer, a paste with a fluorinated oil, or a plate with KBr or NaCl). Padgett *et al.* [38] explained the observed variations by complex formation involving both an anion and a cation.

TABLE 4.

Infra-red spectrum (gas)		Raman spectrum (liquid)		Assigned to [30]
light	heavy	light	heavy	
—	—	3042(10) *p*	2293	$\nu_1(A_1')$
—	—	1132(8) *p*	1077	$\nu_2(A_1')$
—	—	992(7) *p*	987	$\nu_3(A_1')$
—	—	1617.0 *	1586*	$\nu_4(A_2'')$
—	—	1251 *	951*	$\nu_5(A_2'')$
3056	2280	3042(10) *d*	2288	$\nu_6(E')$
1556	1530	1555(3) *d*	1523	$\nu_7(E')$
1410	1283	1410(2) *d*	1282	$\nu_8(E')$
1174	931	1176(2) *d*	935	$\nu_9(E')$
675	667	676(6) *d*	663	$\nu_{10}(E')$
737	577	—	—	$\nu_{11}(A_2'')$
830	861	—	—	$\nu_{12}(A_2'')$
—	—	1031*	846*	$\nu_{13}(E'')$
—	—	340(4) *d*	309	$\nu_{14}(E'')$

* Calculated results.

TABLE 5.

Compound	Symmetry of vibration				Ref.
	E′	E′	A_2''	E′	
1,3,5-Triazine	1555	1410	735	675	26,30
Trideutero-1,3,5-triazine	1530	1284	667	577	30
Trimethyl-1,3,5-triazine	1560	1410	775	—	26
Triethyl-1,3,5-triazine	1560	1387	785	—	26
Cyanuric chloride	1510	1268	735	705	—
Trimethoxy-1,3,5-triazine	1565	1390	814	—	37
Melamine	1560	1434	813	730	46,37
Hexadeuteromelamine	1534	1211	810	—	46
Trisodium cyanurate	1530	1410	828	—	41

TABLE 3*.

Symmetry class	No. of vibrations	Symmetry of vibrations				Activity of vibrations		Character of vibrations
		c_3	σ_x	σ_z	c_y	Raman spectra RS**	IRS***	
A_1'	3	*s*	*s*	*s*	*s*	*p*	*ia*	in plane
A_1''	0	*s*	*as*	*as*	*s*	*v*	*ia*	out of plane
A_2'	2	*s*	*as*	*s*	*s*	*v*	*ia*	in plane
A_2''	2	*s*	*s*	*as*	*as*	*v*	M_z	out of plane
E′	5	*e*	*e*	*s*	*e*	*dp*	$M_\perp$	in plane
E″	2	*e*	*e*	*as*	*e*	*dp*	*ia*	out of plane

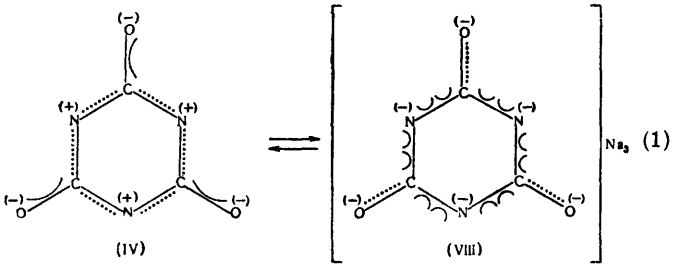
* The symbols used in Table 3 are taken from Kohlrausch's book [25].

** Raman spectra.

*** Infra-red spectra.

No investigations have been made of the vibrational spectra of cyanuric acid in solution, apart from Ito's work[42] on the Raman spectra. He explained the observed changes in the spectra of cyanuric acid in acid and in alkaline solutions by tautomeric changes, although examination of the electronic spectra shows that ions of the tautomeric forms are produced. The frequencies cited by Ito show poor agreement with those obtained from the spectra of the crystals.

Formation of a salt of cyanuric acid involves a redistribution of electron density[41,43,44] accompanied by an increase in multiplicity of the ring C–N bonds and a decrease in that of the C–O bonds. In other words, the structure of the salts corresponds to an ion of the hydroxy-form of cyanuric acid:



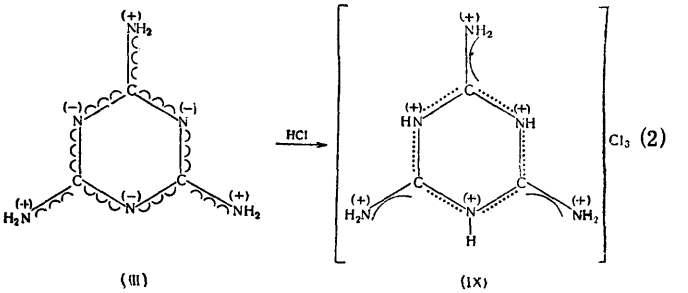
(IV) (VIII) (1)

In agreement with the above scheme (1), the carbonyl band has disappeared from the spectrum of the trisodium salt, and absorption bands characteristic of the 1,3,5-triazine ring (listed in Table 5) have appeared.

In addition to the spectra of the salts, the infra-red spectra of the "amides" of cyanuric acid have been well studied, the spectra of the "triamide", melamine (2,4,6--triamino-1,3,5-triazine)[34,37,45,46], in especial detail.

The infra-red spectrum of melamine contains four absorption bands in the region of the N–H vibrations: two narrow bands of higher frequency 3470 and 3425 cm^{-1}, and two broad bands of lower frequency 3335 and 3120 cm^{-1}. Finkel'shtein[37] assigned the first two bands to antisymmetric and symmetric vibrations of NH_2 groups forming a weak hydrogen bond, while the second pair were assigned to corresponding vibrations of NH_2 groups forming a strong hydrogen bond. Such an assignment explains the frequencies and the form of the absorption bands, and agrees with the view that two types of hydrogen bond are present in cyanuric acid. Jones and Orville-Thomas[46] have given a different assignment of the frequencies: the band at 3470 cm^{-1} was assigned to an antisymmetric vibration of the NH_2 group, the 3425 cm^{-1} band remained unassigned, the 3335 cm^{-1} band was assigned to a symmetric vibration of the NH_2 group, and the 3120 cm^{-1} band was interpreted as a combination band (NH_2 deformation vibration 1640 cm^{-1} plus C–N stretching vibration 1540 cm^{-1}). It can be objected to such an assignment that it is difficult to explain the difference in half-width between antisymmetric and symmetric vibrations of NH_2 groups, while the intensity of the 3120 cm^{-1} band is too great for a combination band. Although the final solution to this problem remains for the future, the observed absorption is linked in both papers with the presence of NH_2 groups of the amino-form of melamine. Such an explanation is consistent both with determinations of interatomic distances and with an examination of the rest of the vibrational spectrum of melamine, in which it is easy to identify all the characteristic bands of the triazine ring (see Table 5).

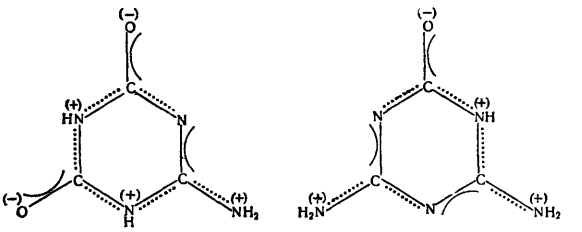
Examination of the infra-red spectra[43] and especially the electronic spectra of salts of melamine shows that salt formation is accompanied by a redistribution of electron density such that the multiplicity of the cyclic C–N_r bonds is diminished, while that of the C–N_ω bonds outside the ring increases, as shown in the scheme (2).



(III) (IX) (2)

Thus melamine trihydrochloride can be regarded as a salt of the imino-form of melamine.

The infra-red spectra have been studied also of the other amides of cyanuric acid: ammelide — 2-amino-4,6--dihydroxy-1,3,5-triazine (X) — and ammeline — 2,4-diamino-6-hydroxy-1,3,5-triazine (XI)[37,47] (see Section 4). The presence of intense bands in the neighbourhood of 1700 cm^{-1} definitely indicates that these compounds have the oxo-structure in the crystalline state. The frequencies associated with the triazine ring fall slightly in the sequence: melamine, ammeline, ammelide. Salt formation takes place according to scheme (1) by reaction with alkalis, and according to scheme (2) by reaction with acids.



(X) (XI)

Among the halogenated derivatives, the vibrational spectra of the mono-, di-, and tri-chlorotriazines have been most fully studied[26,44,45,47-49]. All the spectra show quite distinctly the characteristic absorption bands of the 1,3,5--triazine ring, which are shown in Table 5 for the case of trichlorotriazine. The successive introduction of chlorine atoms greatly affects the band around 1450 cm^{-1}, and to a less extent the bands at 790 and 1560 cm^{-1}. The 847 cm^{-1} band observed in the spectra of the di- and tri-chlorinated derivatives is assigned to a vibration involving the chlorine atoms.

Among other derivatives of 1,3,5-triazine, the spectra have been studied of trimethoxytriazine[37,44], substituted melamines[45], and methoxy-derivatives of triazine[47].

The results obtained from the investigation of the vibrational spectra of 1,3,5-triazine derivatives agree well with data on the molecular structure from determinations of interatomic distances. Especially valuable results have been obtained for cyanuric acid, its amides, and its salts, which have enabled the structure of these molecules to be established for the first time.

4. ELECTRONIC SPECTRA

Investigation of the ultra-violet absorption spectra of 1,3,5-triazine derivatives started more than half a century ago with the work of Hartly[50], who was the first to obtain the spectrum of cyanuric acid in aqueous solution.

Attempts at a theoretical calculation of the delocalisation energy[51] and the electronic spectra[52-54] of 1,3,5-triazine were undertaken long before Grundmann and Kreutzberger identified this compound. Owing to imperfections in the theory and inadequate experimental data, such calculations were, of course, unable to give an accurate prediction of the electronic spectrum of the triazine. Only subsequent improvement in the theoretical equipment enabled an approach to be made to calculating the electronic spectrum of 1,3,5-triazine (Table 6).

As can be seen from Table 6, the origin of the first absorption band is not absolutely clear. Several authors assign it to the triplet $n \rightarrow \pi^*$ ($^1A_1' \rightarrow {}^3A_1'$) electronic transition, whereas other workers assign it to a $\pi \rightarrow \pi^*$ ($^1A_1' \rightarrow {}^1A_2''$) transition. The latter assignment maintains the analogy[60] with the spectrum of benzene, in which the only absorption band in the near ultra-violet range relates[61] to the electronic-vibrational transition $\pi \rightarrow \pi^*$ ($^1A_{1u} \rightarrow B_{2u}$).

The most detailed examination of the problem of assigning electronic transitions by Brinen and Goodman[62] showed that the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions should have similar energies, and probably constitute one absorption band.

Experimental investigation[63] showed the electronic spectrum of 1,3,5-triazine in the near ultra-violet to consist of two bands. The first of them has a sharp maximum at 272 mμ, while the second is located at the limit of sensitivity of quartz spectrophotometers (200–230 mμ), and was not detected in other work[64]. The same applies to the work of Paoloni[65], who detected a second short-wave band in the spectrum of trimethyl-1,3,5-triazine which is absent from the spectra of other alkyltriazines[66,67].

TABLE 6.

Lower excited level		Ref.
symmetry	λ, mμ*	
A_1''	256	54
$^3A_1'$	292	55
$^1A_2'$	234	56
$^1A_2'$	229	57
—	315	58
$^3A_1'$	337	59
Experimental results: origin of band	320	
maximum of band	272	

* For the sake of uniformity and clarity, values in this column have been converted by us from eV into mμ.

Thus only one band can be regarded as reliably established in the spectra of 1,3,5-triazine and its derivatives; the second short-wavelength band requires more careful investigation.

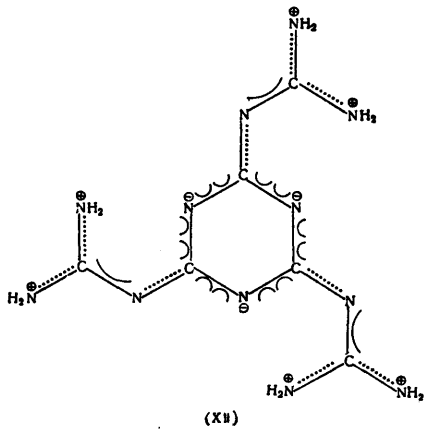
Data on the absorption of trisubstituted triazine derivatives having D_{3h} symmetry are collected in Table 7. A noteworthy feature is the regular shift in band I towards shorter wavelengths accompanied by a decrease in its intensity, roughly in conformity with the decrease in multiplicity of the cyclic C–N bonds (see Table 2). In the spectrum of melamine this band is already represented by a barely perceptible "shoulder" on the background of the intense band III. The existence of such absorption can also be explained by the presence of an ionic form. Band I is absent from the spectrum of cyanuric acid, in which the multiplicity of the bonds in the ring is a minimum. Such behaviour of band I supports its assignment to a $\pi \rightarrow \pi^*$ transition ($^1A_1' \rightarrow {}^1A_2'$). Dewar and Paoloni[71] reached a similar conclusion, after having made the first attempt at a quantum-mechanical calculation of melamine.

The presence of band II in the absorption spectra of 1,3,5-triazine derivatives requires to be verified and more closely specified, as mentioned above. At the present time, therefore, it is pointless to consider it in detail. Little can be said also about the most intense band III, since experimental data on this band are lacking for such fundamentally important compounds as 1,3,5-triazine and its alkyl derivatives.

TABLE 7.

1,3,5-Triazine derivative	Band I		Band II		Band III		Solvent	Ref.
	λ	ε	λ	ε	λ	ε		
Triazine	267	768	221	213	—	—	methanol	63
	268	791	221	137	—	—	acetonitrile	63
	272	881	222	146	—	—	cyclohexane	63
	272	890	—	—	—	—	isooctane	64
Calculated data	292							55
Trimethyltriazine	248	692	227	554	—	—	water	65
	256	795	227	476	—	—	methanol	65
	256	795	—	—	—	—	methanol	66
	264	701	227	289	—	—	cyclohexane	65
Triethyltriazine	259	696	—	—	—	—	methanol	66
Tributyltriazine	259	690	—	—	—	—	methanol	66
Trichlorotriazine	255	680	—	—	—	—	methanol	54
	256*	600	—	—	196.5	450000	water	68
Trimethoxytriazine	258	521	—	—	137	42 000	water	64
Tri(hydroxymethylamino)triazine	250	weak	—	—	213	50 000	water	54
Tris(dihydroxymethylamino)triazine	250	weak	—	—	213	50 000	water	54
Melamine	236	weak	—	—	208	51 000	water	68,69 70,71
Trisdimethylaminotriazine	232	weak	—	—	208	56 000	water	54
Trisdiethylaminotriazine	230	weak	—	—	210	55000	water	68
Cyanuric acid	absent		absent		<170	—	water	68

Where conjugation of the 1,3,5-triazine ring with C=N double bonds occurs, the sole example of which is provided by triguanidinotriazine (XII), a very intense absorption band[72] appears having λ_{max} = 261 mμ and $\epsilon_{max} \simeq 64000$.



(XII)

Triguanidinotriazine not only possesses a greater number of interacting π-electrons than 1,3,5-triazine, but also differs in symmetry, which may be reduced from C_{3h} as far as C_s depending on orientation. It is evidently advisable to regard triguanidinotriazine as a separate chromophore, since different selection rules operate here, and the electron transitions are different in character.

TABLE 8.

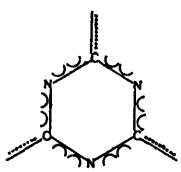
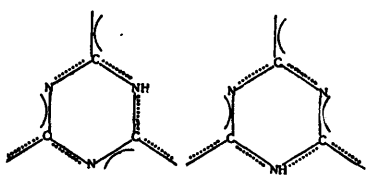
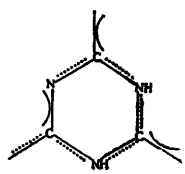
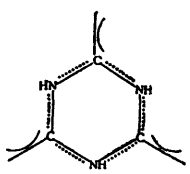
1,3,5-Triazine derivative	Band I		Band II		Band III	
	λ	ε	λ	ε	λ	ε
2-Amino-	261	1960	220	16230	215	25 000
2-Amino-4,6-dichloro-	260	1990	224	15250	215	20 000
2,4-Diamino-	259	3620	absent		205	34 500
2,4-Diamino-6-methyl-	255	3435	absent		205	35 000
2,4,6-Triamino-	236	weak	absent		208	51 000

The same applies to the absorption spectra of derivatives of 1,3,5-triazine containing benzene[73-76] and naphthalene[77] rings, the spectra of which differ in character from those of derivatives of the original triazine.

Changes in the shape of the electronic shell can have a great influence on the nature of the electronic spectrum as is shown by the examples of mono- and di-substituted 1,3,5-triazine[54] (Table 8).

Table 8 gives data on amino-substituted triazines in which the amino-group interact very strongly with the

TABLE 9.

Diagram of molecule	Symmetry	Band	2,4,6-Triamino-1,3,5-triazine (melamine)		2,4-Diamino-6-hydroxy-1,3,5-triazine (ammeline)		2-Amino-4,6-dihydroxy-1,3,5-triazine (ammelide)		2,4,6-Trihydroxy-1,3,5-triazine (cyanuric acid)	
			λ	ε	λ	ε	λ	ε	λ	ε
	D_{3h}	I	236	very low	230	4700	230	7300	228	7500
		III	206	47 200	—	—	—	—	—	—
 a b	C_s, C_{2v}	I	236	10 100	228	7500	226	8500	222	7500
		II	210	35 000	202	22 000	198	21 000	198	16 000
		III	190	4000	170	40 000	185		—	—
	C_s	I	230	22 000	230	19 800	220	12 500	215	10 500
		III	—	—	196	45 000	180	38 000	182	35 300
	D_{3h}	III	weak absorption without maxima down to λ < 170 mμ							

1,3,5-triazine ring. Although the marked differences produced in the spectra on successive replacement of the hydrogen atoms of the triazine by amino-groups are quite clearly evident in Table 8, the lack of data on absorption in the vacuum ultra-violet range does not allow a complete picture to be obtained of the influence of amino-groups.

Considerably more complete information is available on the absorption spectra of cyanuric acid and its amides, ammeline (XI), ammelide (X), and melamine (III) (Table 9). The changes occurring in the absorption spectra of these compounds in acid and alkaline media were previously linked by several workers[69,70,78,79] with tautomeric changes of the lactam–lactim type. Later work[81,82] has shown, however, that ionisation takes place at the same time, so that the final result of the process is the ion of the corresponding tautomeric form.

Table 9 shows diagrams of the molecular structure of these molecules or ions omitting the charges and external atoms. Data on the absorption spectra of neutral molecules, the structures of which have been reliably established from their infra-red spectra[37,43], are given diagonally across Table 9, inside the rectangles formed by the heavy lines. The horizontal rows in the table correspond to successive replacement of amino- by hydroxy-groups (moving from the left to the right). The vertical columns correspond to successive increase in positive charge on the cations or a corresponding decrease in negative charge on the anions (moving down the table).

The data in Table 9 show a clear similarity in the spectra of ions and molecules over a whole horizontal series, indicating a similarity in molecular structure expressed by a diagram common to the whole series.

Hence it can be seen that the formation of positive ions is accompanied by the elimination of one double bond from the ring, whereas the formation of negative ions introduces an additional double bond into the ring. Thus the structure of the corresponding ion can be readily established from that of the neutral molecule.

It follows also from Table 9 that the character of the absorption of amino- and hydroxy-derivatives of 1,3,5-triazine is determined solely by the distribution of the electron cloud of the triazine ring. The presence of charges and differences in external functional groups somewhat distort the shape of the absorption curve, but the general character of the spectrum remains unchanged.

Similarity in absorption spectra can probably be traced in several other derivatives of 1,3,5-triazine. For example, there is a striking analogy between the spectra of monoamino-1,3,5-triazines (Table 8) and the second series in Table 9. Here, with the same general character of the spectra (three maxima), the difference consists solely in a shift in the wavelengths of the absorption maxima.

Apart from the electronic absorption spectra, increasing attention has been paid recently to research on the luminescence of 1,3,5-triazine[83,84] and its derivatives[85]. Further development of research in this field, as on other types of electronic spectra, undoubtedly promises to give much new information from which details of the electronic structure of these molecules can be assessed.

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Although problems of the molecular structure of 1,3,5-triazine and its derivatives, in particular of the most important of their amino- and hydroxy-derivatives, have now been solved in the sense of the relative arrangement of the atoms having been established, questions associated with the nature and the properties of the bonds which are formed remain open to a considerable extent. The information required for solving these problems too is now being rapidly collected. As far as spectroscopic investigations are concerned, this process is accelerated by their great practical value. Thus ultra-violet and infra-red spectra have already been employed for a long time for analytical purposes[80,86-90], directly for the solution of purely technological problems, and also for studying various physico-chemical properties (for example, ionisation constants and thermodynamic functions). New data are accumulated mainly by extending the range of substances studied. However, it is more important for the development of theoretical research to make exact investigations of a limited number of compounds having the simplest structure. The simplest representative of this class of compounds, 1,3,5-triazine itself, requires accurate determination of the ultra-violet spectra, including the vacuum ultra-violet, and study of the microwave spectrum in order to ascertain the exact interatomic distances.

The collection and extension of experimental data will undoubtedly require the development of theoretical methods and concepts, for which 1,3,5-triazine is almost as important as benzene has been in its time. The theoretical papers containing calculations on 1,3,5-triazine which are now appearing represent the first steps in the creation of a modern theory of molecular structure. All the effort which has been put into the study of the structure of its derivatives is justified by their great value in modern technology, which promises to contribute greatly to an understanding of the origins of the properties which they confer on plastics (incombustibility, heat-resistance, stability, etc.) and the possibility in due course of combining these properties.

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