Crystal Structure and Spectroscopic Analysis of Melamine Hydrobromide. Evidence for *iso*-Melamine Cations and Charge–Transfer Complexes in the Solid State

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The crystal structure and vibrational analyses of melamine hydrobromide by FTIR and FT-Raman spectra, are presented. The crystallographic data show π-electron delocalization towards the amino substituents with ring nitrogen protonation in the solid state. Additionally, the presence of intermolecular hydrogen bonding interactions occurring between amino substituents and ring nitrogen lone-pairs gives rise to charge–transfer complexes, as demonstrated by UV–VIS reflectance in the solid state. FTIR and FT-Raman spectra allow the assignments of the vibrational modes in melamine hydrobromide by comparison with the corresponding deuteriated molecules, and show the existence of *iso*-melamine cations in the solid state.

Many 1,3,5-triazine derivatives have been the subject of theoretical and practical interest in past years.[1] In particular, its hydroxy and amino derivatives have become of increasing importance in plastics as flame retardants, heat resistants and incombustibility agents.[2] Their prominent physicochemical properties are characterized by strong interactions between the π-electrons of the triazine ring and the lone-pairs of the nitrogen atoms of the substituents.[3] Another interesting feature which is supported by crystallographic and spectroscopic evidence, consists of the formation of imino (*iso* forms) and *oxo* forms in the solid state for amino and hydroxy substituted triazine, respectively. It has been demonstrated that 2,4,6-triamino-*s*-triazine (melamine) shows a slight difference in bond lengths in the triazine ring with a lowered symmetry for the crystal field interactions due to the formation of intermolecular arrangements by the hydrogen atoms, which are consistent with the presence of the amino-form in the crystalline state.[4] In contrast, the notable feature of the cyanuric acid structure is the localization of the double bonds on the substituents to form three carbonyl groups for tautomeric migration of hydrogen atoms of the ring nitrogen atoms (*oxo* form).[5] Although spectroscopic studies and the crystal structure of melamine and many of its derivatives have been reported in the past years,[6–9] there has been no detailed work dealing with vibrational assignments, crystal structure and the UV–VIS spectra of melamine hydrobromide which attempts to verify the existence of the *iso* form in the solid state.

Melamine hydrohalides have industrial relevance since they are claimed to impart fire retardant properties to polypropylene.[10,11] It has recently been shown that melamine hydrobromide becomes a very efficient fire retardant for polyolefins in combination with small amounts of free radical initiators.[12] In addition, the thermal behaviour of melamine hydrobromide has shown a synergistic effect in the presence of bismuth and antimony oxides in smoke suppression effectiveness in polyolefins.[13]

Our contribution reports the results of crystal structure investigations indicating the presence of *iso*-melamine cations and strong hydrogen bond interactions with the formation of intermolecular charge–transfer complexes in the solid state. The UV–VIS spectra confirm these interpretations, and from the frequency assignments of the vibrational spectra have been obtained a comparison of the corresponding deuteriated molecule.

This paper continues an investigation of the electronic structure and vibrational assignments of melamine hydrobromide in the solid state, chosen in accordance with our previous work on guanylurea hydrochloride because of its strong electronic similarity and behaviour exhibited in the solid state.[14] In addition, the spectroscopic and crystallographic properties of melamine hydrobromide have been used as a support for analytical purposes by understanding its photothermal reactivity in the bulk polymer.

Experimental

Materials.—All solvents and reagents were purchased from Aldrich and used as received. Melamine hydrobromide was obtained by hydrobromic acid (37%) addition (5 cm³) to a stirred, boiling aqueous solution of melamine. After being cooled, the resulting white powder was washed with boiling methanol and dried *in vacuo*. Recrystallization was achieved by dissolution in an ethanol–methanol (1:1) mixture. (Found: C, 17.4; H, 3.4; N, 40.6. Calc. for $C_3H_7N_6Br\cdot0.5H_2O$, C, 17.40; H, 3.41; N, 40.59%). The complete and stable deuteriated compound was obtained by repeatedly refluxing in deuterium oxide solution.

Crystal Data.—$[C_3H_7N_6]^+\cdot Br^-\cdot0.5H_2O$, $a = 4.757(1)$, $b = 16.815(4)$, $c = 9.423(2)$ Å, $\beta = 99.12(2)°$, $V = 744.2(3)$ Å³ (by least-squares refinement on diffractometer angles for 25 automatically-centred reflections in the range $(7 \leqslant \theta \leqslant 13°)$, space group $P2_1/m$ (No. 11), $Z = 4$, $D_c = 1.928$ g cm⁻³. Colourless crystals of dimension $0.14 \times 0.28 \times 0.34$ mm; $\mu(\text{Mo-K}\alpha) = 54.13$ cm⁻¹.

Data Collection and Processing.—CAD4 diffractometer, $\omega/2\theta$ scan technique, graphite-monochromated (Mo −Kα) radiation ($\lambda = 0.710\ 69$); 1674 unique reflections measured $(2 \leqslant \theta \leqslant 27°$; $+h$, $+k$, $\pm l)$, of which 1133 with $I \geqslant 3\sigma(I_0)$ are used in the refinement. All data were corrected for Lorentz, polarization and absorption (minimum transmission factor, 0.62).

Structure Analysis and Refinement.—Solution was by direct methods (MULTAN82).[15] Full matrix least-squares refinement was used with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic (except the water hydrogens, which,

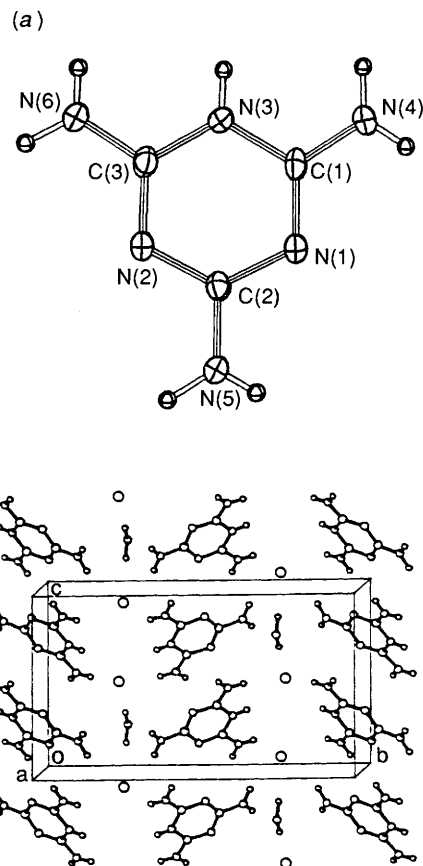**Table 1** Positional parameters ($\times 10^4$; $\times 10^3$ for hydrogen atoms) with esds in parentheses

N(1)	7195(7)	174(2)	3407(4)
N(2)	3284(7)	182(2)	1438(4)
N(3)	4086(7)	−910(2)	2982(4)
N(4)	7905(7)	−949(2)	4791(4)
N(5)	6384(8)	1215(2)	1843(4)
N(6)	352(7)	−906(2)	1134(4)
C(1)	6452(8)	−548(2)	3740(4)
C(2)	5597(8)	511(2)	2248(4)
C(3)	2571(8)	−538(2)	1834(4)
Br(1)	6745(1)	2500	5092.3(7)
Br(2)	3828(1)	2500	−883.5(7)
O(1w)	960(10)	2500	2291(6)
H(3)	365(7)	−133(2)	325(4)
H(41)	913(8)	−73(2)	520(4)
H(42)	740(7)	−141(3)	498(4)
H(51)	755(8)	142(3)	231(4)
H(52)	560(9)	145(3)	100(5)
H(61)	−64(7)	−68(2)	38(4)
H(62)	7(7)	−135(3)	132(4)
H(1w)	207	250	139
H(2w)	250	250	305

Table 2 Bond distances/Å and bond angles/° with esds in parentheses

N(1)–C(1)	1.316(5)
N(1)–C(2)	1.352(5)
N(2)–C(2)	1.354(5)
N(2)–C(3)	1.327(5)
N(3)–C(1)	1.376(5)
N(3)–C(3)	1.354(5)
N(4)–C(1)	1.302(5)
N(5)–C(2)	1.316(5)
N(6)–C(3)	1.308(5)
C(1)–N(1)–C(2)	116.2(3)
C(2)–N(2)–C(3)	115.8(3)
C(1)–N(3)–C(3)	119.9(3)
N(1)–C(1)–N(3)	120.8(3)
N(1)–C(1)–N(4)	121.9(4)
N(3)–C(1)–N(4)	117.2(3)
N(1)–C(2)–N(2)	125.9(3)
N(1)–C(2)–N(5)	117.5(4)
N(2)–C(2)–N(5)	116.6(4)
N(2)–C(3)–N(3)	121.2(3)
N(2)–C(3)–N(6)	120.8(4)
N(3)–C(3)–N(6)	118.0(3)

(a)

(b)

Fig. 1 (a) ORTEP view of the [H·Melamine]$^+$ cation showing the thermal ellipsoids at 30% probability. (b) Crystal packing of the compound [H·Melamine]$^+$·Br$^-$·0.5H$_2$O.

The FTIR spectra were carried out on a Bruker IFS88 spectrometer in KBr pellets with a resolution of 2 cm^{-1} and at least 400 scans.

Results and Discussion

Crystallographic Analysis.—Final atomic positional parameters are reported in Table 1. Bond distances and bond angles are given in Table 2; an ORTEP [19] view of the [H·Melamine]$^+$ cation is shown in Fig. 1(a) and the crystal packing is given in Fig. 1(b). Tables of hydrogen atom coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.* The crystal structure consists of [H·Melamine]$^+$ cations linked to each other around centres of symmetry by means of N–H···N hydrogen bonds to form infinite ribbons, laterally solvated by Br$^-$ anions and water molecules, both situated on crystallographic m planes. The scheme of the three-dimensional net of hydrogen bonds is shown in Fig. 2 and the structural parameters are given in Table 3. The [H·Melamine]$^+$ chains are approximately situated on the xy plane and staked along the c axis. The protonated triazine ring is almost planar [$(\Delta/\sigma)^2 = 40.7$] with the largest deviations from the least-squares plane through the six ring atoms of only −0.011(4) and 0.017(4) Å for N(1) and C(1) atoms, respectively. The deviations of the amine nitrogens are 0.071(4), 0.047(4) and −0.013(4) Å for N(4), N(5) and N(6), respectively. However, the distance between the rings along the c axis of 0.5 c (ca. 4.71 Å) prevents any interaction between their π-electron densities.

The consequence of the protonation of N(3) nitrogen results

owing to their instability during the refinement, are kept fixed in the positions found in the ΔF map). The weighting scheme $\omega = 4F_0^2/[\sigma^2(F_0^2) + (0.04F_0^2)^2]$ with $\sigma(F_0)$ from counting statistics gave satisfactory agreement analyses. Final R and R_w values are 0.032, 0.040; max shift/error = 0.03; largest ΔF peak 0.30 e Å^{-3}; S (esd of an observation of unit weight) = 1.347. All calculations were performed using the CAD4-SDP [16] and PARST [17] systems of programs; scattering factors are from ref. 18.

Spectroscopic Measurements.—The Raman spectra of powders were measured in a Pyrex glass tube by using a FRA 106 FT-Raman accessory mounted on a FTIR IFS66 optical bench. The Nd:YAG laser line used was at 1064 nm. The spectral resolution was set at 3 cm^{-1} throughout with the laser power at 300 mW for at least 200 scans. The scattered radiation was collected with a geometry of 90° from the sample and passed throughout the filter module to remove the unshifted Raleigh scattering and then focused into the FTIR optic bench and the interferometer. Each spectrum was corrected by subtraction of the fitted baseline with a polynomial function. The Raman spectra of deuteriated compound were recorded under the same conditions.

Table 3 Hydrogen bond parameters. Distances/Å and angles/°

D–H···A	Symmetry operator[a]	D–A	D···A	H···A	D–A···A
N(3)–H(3)···Br(1)	II	0.79(4)	3.290(4)	2.54(4)	160(3)
N(4)–H(41)···N(1)	III	0.74(4)	2.960(4)	2.22(4)	174(3)
N(4)–H(42)···Br(1)	II	0.84(5)	3.433(3)	2.68(4)	149(3)
N(5)–H(51)···O(1w)	IV	0.74(4)	3.049(5)	2.44(5)	142(4)
N(5)–H(52)···Br(2)	I	0.91(4)	3.429(4)	2.55(5)	162(4)
N(6)–H(61)···N(2)	V	0.88(3)	3.003(5)	2.13(3)	176(3)
N(6)–H(62)···Br(2)	V	0.78(5)	3.323(3)	2.67(4)	143(4)
O(1w)–H(1w)···Br(2)	I	1.07	3.479(6)	2.42	170
O(1w)–H(2w)···Br(1)	I	0.94	3.498(5)	2.56	179

I: x, y, z; II: $1 - x, -y, 1 - z$; III: $2 - x, -y, 1 - z$; IV: $1 + x, y, z$; V: $-x, -y, -z$.
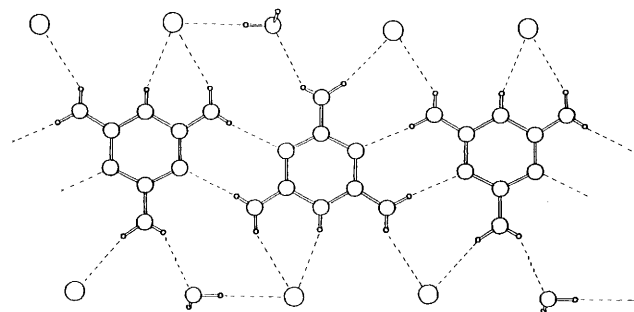
Fig. 2 Hydrogen bond scheme showing a ribbon of [H·Melamine]$^+$ cations laterally solvated by Br$^-$ anions and water molecules
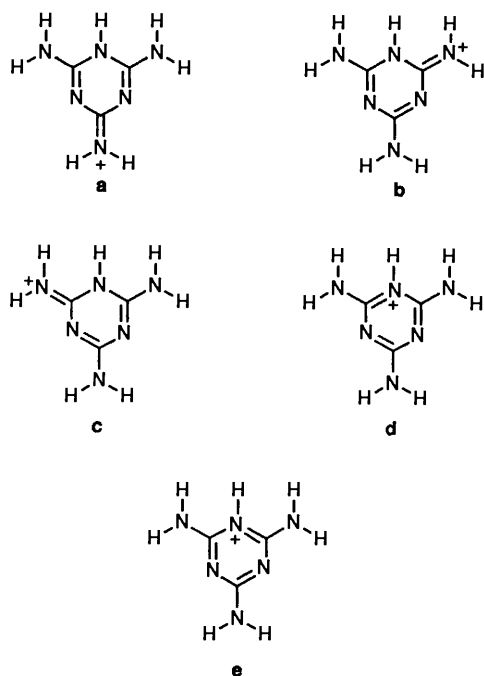
Fig. 3 Possible canonical forms contributing to the electronic ground state of the cation

in a dramatic variation of bond distances and angles over the whole cation with respect to the neutral melamine molecule.[4] By comparing the two crystal structures it is evident that out of all the possible canonical forms contributing to the ground state of the cation (Fig. 3), the forms **a–c** seem to be the most important, owing to the accentuated quinoid character of the ring and the short C–NH$_2$ bond distances. As a consequence of π-electron density delocalization, the positive charge is distributed almost uniformly over the N(3)–H, N(4)–H$_2$, N(5)–H$_2$ and N(6)–H$_2$ groups, favouring their involvement in hydrogen-bond interactions. The strength of the paired N–

H···N hydrogen bonds [with N···N distances of 2.960(5) and 3.003(5) Å] is probably related to the formations of rings where two hydrogen bonds become stronger, through a mechanism by which they are reinforced through resonance.[20] This situation can be found in other related molecules, i.e. 6-methylisocytosine[21] and in 2,6-diaminopyrimidin-4(3H)-one[22] where N···N hydrogen bond distances are 2.973(3) and 2.987(3) Å, respectively. As regards the internal C–N–C angles, we note that in neutral melamine these angles have an average value of 114.5°, while in the present compound the angle at the protonated N(3) atom is 119.9(3)° and those at the N(1) and N(2) atoms, bearing lone pairs of electrons, are 116.2(3)° and 115.8(3)°. These situations are easily explained in terms of valence shell electron pair repulsion (VSEPR) theory. Likewise, the biprotonated melamine [H$_2$·Melamine]$^{2+}$, whose crystal structure has been recently determined as a molecular complex with cyanuric acid,[23] presents similar angular features, the C–N–C internal angles at the protonated nitrogens being 119.3(4)° but the angle at the non-protonated nitrogen being 116.2(3)°.

Spectroscopic Analyses.—According to the reported crystal structure (Figs. 1 and 2) melamine cations are significantly distorted from the ideal hexagonal form and as such belong to no symmetry group in the solid state. The enhanced π-electron delocalization towards substituents is in favour of a quasi co-planarity of amino groups and triazine ring, thus indicating that, at least in dilute aqueous solution, it could belong to a C_s symmetry group. The frequency assignments (Table 4) of melamine hydrobromide have been obtained by comparing the spectra of melamine hydrobromide with the corresponding deuteriated compound and with guanylurea cations to observe the similarity in their structural and π-electron delocalization similarity.

In the –NH stretching region (Figs. 4 and 5) the higher frequency bands at 3379, 3344 and 3256 cm^{-1} have been attributed to the symmetric stretching vibration modes, while the lower frequencies at 3112 and 2960 cm^{-1} in the IR spectrum are assigned to the asymmetric ones. These assignments have been confirmed from shifts following deuteriation in the Raman and IR spectra of the corresponding deuteriated compound. The broad nature and the splitting of these bands indicates strong hydrogen-bond interactions with the neighbouring cations in the solid state. Further evidence regarding these interactions is reported in Fig. 8, where the UV–VIS reflectance spectrum (solid line) shows the formation of three bands in the solid state occurring at 300, 328 and 378 nm, which disappear in the aqueous solution transmittance spectrum (dashed line).[24]

These results have been attributed to the formation of π-electron charge–transfer complexes in the solid state by hydrogen bond interactions as shown in Fig. 2.

The in-plane vibration modes of –NH$_2$ (Figs. 6 and 7) groups occurring at 1179 and 1159 cm^{-1} (doublet) and at 1714 cm^{-1} in the IR spectrum, have been assigned to rocking ρ(NH$_2$) and

Table 4 Vibrational assignments of melamine hydrobromide[a]

Melamine		Melamine hydrobromide				
IR (solid)	Raman (solid)	IR (solid)	Raman (solid)	IR (deuteriated solid)	Raman (deuteriated solid)	Assignments[b]
3469vs	3470w	3379vs	3354w	2544ms	2538m	
3418vs	3420wb	3344vs		2522ms	2518sh	$v_s(NH_2)$
3334vb	3353w	3295vs	3271w	2463m	2464w	
					2443w	
3200sh	3210sh		3192mw	2354vs	2378wb	
3125vs		3112vs	3123wb	2317vs	2310wb	$v_{as}(NH_2)$
3149vs		2960s	2959sh	2270vs	2277sh	
1653vs						
	1670w	1714s	1693mw	1265mw	1273w	$\delta(NH_2)$
1630sh						
		1678vs	1660m	1682s	1643mb	
		1648vs	1633w			$v(C = N)$
		1620s	1603m	1655s	1623mw	
1580sh	1576w					
	1572w	1556m	1560wb	1594sb	1580mb	$v_1(CN)$ ring
1550vs	1551m					
1467ms	1456w	1490sb	1509w	1473sb	1493mw	$v_2(CN)$ ring
1436s	1443w	1411w	1486sh	1400w	1460sh	$v_3(CN)$ ring
		1361m	1373vw	1068mw	1077vw	$\delta(NH)$
		1333m	1339m	1322w	1327w	$v_4(CN)$ ring
1195w		1179mw	1189m			
	1188w			827wb	827w	$\rho(NH_2)$
1172w		1159mw	1165m			
	1025w	1005w	1008vw	1006w	1013w	
1026mb						ring breathing
	984m	982w	985m	974w	977m	
814ms	814vw	776m		775m		δ ring 'iso-form'
767w	772m	755mb		565mb		$w(NH)$
734w	735w	723vm	730vw	730w	730w	γ ring
		670sh	689vs	646w	653vs	
619mb		635mb	581	462w	410wb	$w(NH_2)$
580m	582w	573w	558mb	552sh	563mw	$\delta(CN)$ subst.
493mb	440w	500mb	497w	518w	504w	$\delta(CN)$ subst.
					474vw	
	390sh				377w	
			387m			$\delta(CN)$ subst.
	377m				347w	

[a] Legends for intensities: s = strong; m = medium; w = weak; v = very; sh = shoulder and b = broad. [b] See ref. 8.

bending $\delta(NH_2)$, respectively.[8] The $\delta(NH_2)$ assignment has been assigned by comparison with some results obtained on guanylurea cations in which the involvement of skeletal modes by mechanical interactions has been suggested.[14] It is worth noting that the bands occurring at 1660, 1633 and 1603 cm^{-1} in the Raman spectrum have been attributed to the stretching vibration of C=N, v(C=N), belonging to either amino substituents or the triazine ring in accordance with the possible canonical structures shown in Fig. 3. The other characteristic bands of the triazine ring, v_1, v_2, v_3 and v_4, are only slightly affected by ring nitrogen protonation and the assignments are the same as those suggested for melamine. By comparison with melamine vibrational spectra a new band at 1333 cm^{-1} in the IR and at 1339 cm^{-1} in the Raman spectrum has been assigned to $\delta(NH)$ vibration modes as reported for guanylurea cations and for the shift in the corresponding deuteriated compound. The ring breathing vibration mode has been found at 985 cm^{-1} with an expected medium intensity in the Raman spectrum, while the ring-bending mode has been attributed to the band at 776 cm^{-1} which is characteristic of the iso form.[25] In the IR spectrum of melamine this band has been observed at 814 cm^{-1} with a sharp medium intensity, while in melamine hydrobromide it moves to 776 cm^{-1} when the

triazine is in the iso form with less than three double bonds in the ring and at least one double bond external to the ring, in accordance with the possible canonical structures reported in Fig. 3. Further investigation on the band at 775 cm^{-1} has been reported in the IR spectra of N-alkyl melamines, ammeline and thioammeline in which the presence of the iso form indicating the protonation of a ring nitrogen has been demonstrated.[25]

Two broad bands occurring at 755 and 635 cm^{-1} which are shifted to 565 and 462 cm^{-1} in the IR spectrum of the corresponding deuteriated cation have been assigned to wagging vibrations modes of –NH, w(NH), and of –NH$_2$, w(NH$_2$) groups, respectively. The other remaining skeletal vibration modes at 573 and 500 cm^{-1} in the IR spectrum and that at 387 cm^{-1} in the Raman spectrum have been tentatively attributed to in-plane bending of CN side groups, v(CN)$_{subst}$ because these remain unshifted on deuteriation.
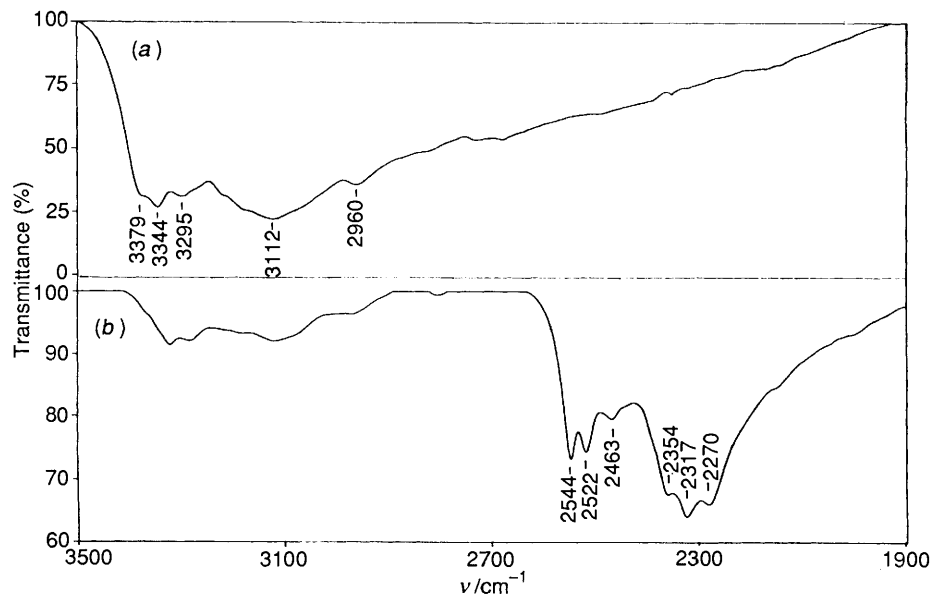
Acknowledgements

Fig. 4 FTIR spectra in the –NH stretching region of melamine hydrobromide (*a*) undeuteriated and (*b*) deuteriated compound
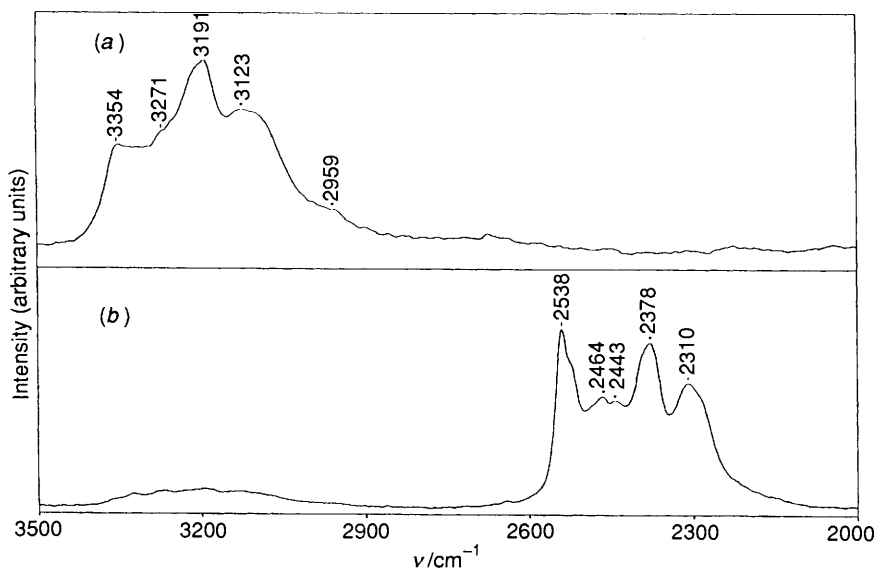
Fig. 5 FT-Raman spectra in the –NH stretching region of melamine hydrobromide (*a*) undeuteriated and (*b*) deuteriated compound
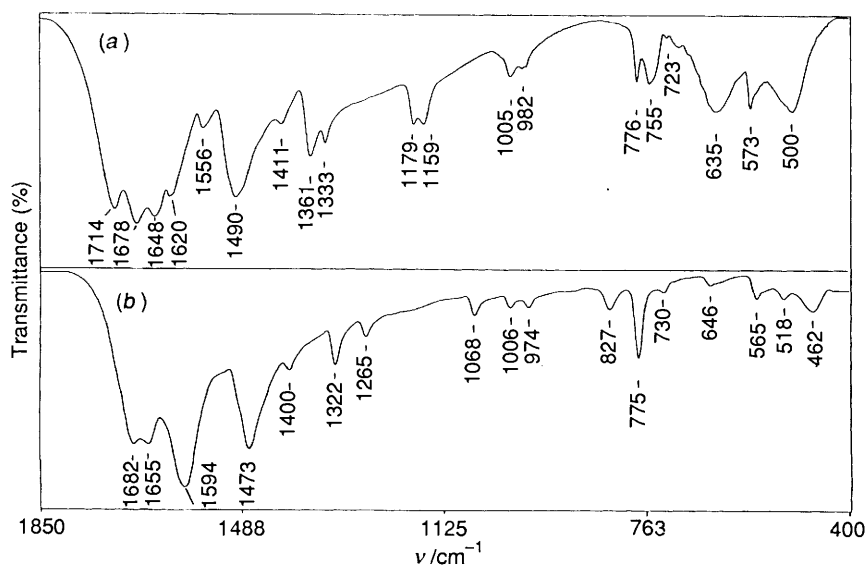
Fig. 6 FTIR spectra of in-plane and out-of-plane vibrations modes of melamine hydrobromide (*a*) undeuteriated and (*b*) deuteriated compound
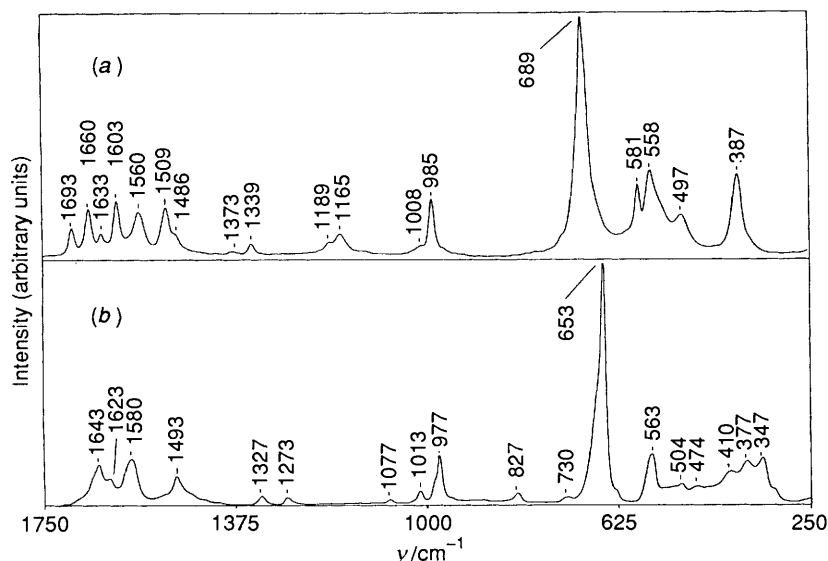
Fig. 7 FT-Raman spectra of in-plane and the out-of-plane vibrations modes of melamine hydrobromide (a) undeuteriated and (b) deuteriated compound
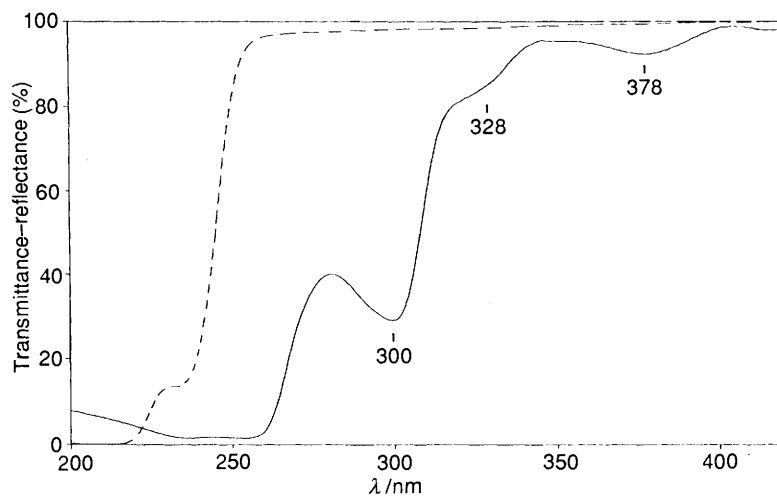

Fig. 8 UV–VIS spectra of the melamine hydrobromide of powder reflectance (solid) and of a 2% (w/w) aqueous solution transmittance (dashed)

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