Nitrogen-14 NQR in s-Triazine Derivatives *

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Within a study of the temperature dependence of NQR frequencies in some s-triazine derivatives [1], resonance frequencies at 4.2 K were determined in melamine, cyanuric acid, and cyanuric chloride. New lines, which were not reported so far, were detected in two of these compounds. In melamine, nine more lines were found as already described in [4]. In cyanuric chloride, two more lines were found showing a second nitrogen site, in agreement with the existence of two chlorine NQR sites in this compound.

Introduction

This paper reports on measurements performed on some s-triazine derivatives, melamine, cyanuric acid, and cyanuric chloride. In a paper by Stutz and Early [1] presented at the 7th ISNQRS, in Kingston, Ont., 1983, initial results concerning the temperature dependence of nitrogen-14 NQR frequencies and relaxation time T_2^* in several derivatives of the s-triazine series including the compounds cited above were reported. It appears that the frequency shifts, when the temperature is raised from 77 to 300 K, are fairly small for several members of the series as compared with the shifts for other nitrogen compounds such as hexamethylenetetramine [2]. This is consistent with the high melting temperature (> 300 C) of the compounds indicating that strong intermolecular forces in the solid limit the amplitude of thermal motion. A further comment is possible considering Table 1, where the average frequency shifts (averaged over the several available lines for each compound) between 77 and 300 K, as derived from the diagrams in [1], are shown together with the value for hexamethylenetetramine.

The compounds listed in Table 1 fall into two groups: the first three compounds are characterized by a small frequency shift while the shifts for the other three are larger. This can quite reasonably be related to the fact that the first three compounds can form intermolecular hydrogen bonds limiting the amplitude of thermal oscillations.

Table 1. Average nitrogen-14 NQR frequency shifts between 77 and 300 K for some s-triazine derivatives together with the melting temperatures

	$\Delta\nu$/kHz	m.p./C
Melamine	7	354 d
Cyanuric acid	13	> 360
Trichloromelamine	18	> 300
Cyanuric chloride	38	~ 148
Trichloroisocyanuric acid	70	~ 250
Hexamethylenetetramine	101	~ 290 sub

To get more information about the temperature dependence of the nitrogen-14 quadrupole coupling constant in these compounds, we carried out measurements at 4.2 K, keeping in mind that the corresponding increase in the Boltzmann factor can be helpful in the detection of lines expected from the chemical structure but unreported so far.

Results

1. Melamine

In this compound only one line was known until recently, which was first reported by Widman [3]. During a search carried out at 4.2 K on a standard cw, Robinson type, spectrometer and completed by further investigation at 173 K on a pulsed spectrometer, it was possible to find nine new lines and obtain a fairly complete set of results, which are

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described in a very recent publication [4]. Observation of some of the ν_d lines makes it possible to pair some of the ν_+ and ν_- lines as $\nu_d = \nu_+ - \nu_-$; frequencies and quadrupole constants at 4.2 and 77 K, respectively, are shwon in Tables 2 and 3.

These results are discussed in [4]: Consideration of the quadrupole coupling constants thus determined, with the help of results previously obtained in s-triazine, pyridine, and aminopyridines leads to the assignment of the lines to the heterocyclic and amino nitrogen atoms shown in the Tables. The quadrupole coupling constants of the amino nitrogen atoms in melamine are not much different from those in the aminopyridines; on the other hand, the quadrupole coupling constant, $e^2 Qq$, of the heterocyclic nitrogen atom in melamine is much lower than it is in pyridine, and the asymmetry parameter, η, is much larger, almost equal to one. In other words, the heterocyclic nitrogen atom is very sensitive to the electron releasing character of the amino groups in the molecule and the conjugation with other heterocyclic nitrogen atoms in the ring. As a matter of fact, the labelling of the x, y and z principal axes of the EFG tensor at the site of the heterocyclic nitrogen atom nuclei, according to the standard convention, $|V_{xx}| < |V_{yy}| < |V_{zz}|$, is different in melamine from what it is in pyridine. In the latter, the Oz axis is directed along the molecular axis of symmetry in the molecular plane whereas Ox is also in the molecular plane and Oy perpendicular to it. In melamine, the labelling of the Ox and Oy axes is interchanged, and, since η is close to one, the labelling of the Oy and Oz axes can also be interchanged or not, depending on whether η is greater than one or smaller, a point that cannot yet be cleared up.

Table 2. Nitrogen-14 NQR frequencies and quadrupole coupling constants in melamine at 4.2 K, in MHz (from ref. [4]; H = heterocyclic and A = amino nitrogen atom).

	ν_+	ν_-	ν_d	$e^2 Q q$	η
H	2.588_4	1.302_6	1.285_8	2.594_0	0.9914
	2.505_8	1.348_2	1.157_6	2.569_3	0.9011
A	2.835_3	2.169_8	av.		
	2.799_5	2.026_0	values:	3.277	0.439

Table 3. Nitrogen-14 NQR frequencies and quadrupole coupling constants in melamine at 77 K, in MHz (from ref. [4]; H = heterocyclic and A = amino nitrogen atom).

	ν_+	ν_-	ν_d	$e^2 Q q$	η
H	2.857_3	1.301_1	1.286_2	2.592_3	0.992_3
	2.505_3	1.346_2	1.159_2	2.567_6	0.902_9
A	2.836_6	2.169_0	av.		
	2.797_7	2.027_8	values:	3.277	0.439

Table 4. Nitrogen-14 NQR frequencies and quadrupole coupling constants in cyanuric acid and cyanuric chloride at 4.2 K, 77 K and room temperature (frequencies are given in MHz).

		ν_+	ν_-	$e^2 Q q$	η
Cyanuric acid	4.2 K	2.793_0	2.037_0	3.199 (av)	0.448 (av)
		2.785_5	1.981_5		
	77 K	$2.790_6^{(1)}$	$2.039^{(1)}$	3.198 (av)	0.486 (av)
		$2.783_5^{(1)}$	$1.980_5^{(1)}$		
	294.7 K	2.780_5			
		2.770_0			
	299.1 K		2.043_8		
			2.001_7		
Cyanuric chloride	4.2 K	3.083_5	3.047_9	4.087_6	0.0174
		3.022_5	2.984_4	4.004_6	0.0190
	77 K	$3.080_0^{(1)}$	$3.044_1^{(1)}$	4.082_7	0.0176
		3.014	2.982	3.997	0.0160
	292.1 K	3.044_1	3.014_9	4.039_3	0.0145
		2.986_2	2.953_7	3.959_9	0.0164

2. Cyanuric Acid and Cyanuric Chloride

In cyanuric acid at 4.2 K, four lines corresponding to those known at 77 K were recorded (Table 4). For one of them a small frequency increase is observed when the temperature rises from 4.2 to 77 K. The four lines were also recorded at room temperature and the frequency of the two ν_- lines is higher than at 77 K.

In cyanuric chloride, the spectrum first reported by Kojima and Minematsu [5] is now completed by two more lines, one ν_+ and one ν_-. The nature, ν_+ or ν_-, of the lines was checked by observing the Zeeman effect on the powder and the pairing unambiguously results from the relative position of the lines in the spectrum. All the lines were recorded at 4.2, 77 K and room temperature (Table 4), and for all of them the frequency decreases as the temperature increases. The observation of two new lines in this compound is an interesting result as it is consistent with the existence of two lines in the chlorine-35 spectrum [6].

Discussion

Effect of hydrogen bonding (HB) on nitrogen-14 quadrupole coupling constants (qcc) is an important question. It is often difficult to get precise information about the extent of the corresponding changes in e^2Qq and η. In some special cases such as complexes of pyridine, with chloroform in particular [7], it is experimentally possible to determine the qcc shift observed when passing from uncomplexed pyridine to the complex and, using the standard Townes and Dailey (TD) theory, to get an estimate of the apparent electronic charge transfer from the nitrogen atom lone pair orbital in pyridine towards the proton (0.05 electron in the case of chloroform).

The case of melamine is more complicated as hydrogen bonding occurs between the melamine molecules themselves and it is not clear how one can experimentally obtain the nitrogen qcc's in the free molecule. HB in melamine can be expected to be strong from the high melting temperature (354 C) of the compound as compared to that of cyanuryl chloride (154 C), a related compound in which no HB is present. On the other hand, nitrogen is usually considered as a weak proton acceptor for the formation of HB though its electronegativity in melamine is increased by conjugation as compared to that in the aminopyridines which are used as a basis for the discussion in [4].

It is clear that in the frame of the TD theory HB can explain the lowering of e^2Qq and increase of η of the heterocyclic nitrogen atoms in melamine. Such a situation is experimentally illustrated by the pyridine · pyrrole complex in which $e^2Qq = 4.287$ MHz and $\eta = 0.48$, values to be compared with those, 4.60 MHz and 0.39 in uncomplexed pyridine [8]. A plain calculation taking into account only HB in melamine leads to a depletion of 0.44 electron of the lone pairs of the heterocyclic nitrogen atoms from the observed lowering in e^2Qq and to an η value of 0.78 less than the experimental value of 0.95 but not too far of it considering the roughness of the model used.

If HB should considered as the major contribution to the changes observed in the qcc's of the heterocyclic nitrogen atoms in melamine, it should also be considered as the major contribution to the changes observed when passing from pyridine to aminopyridines and, to be consistent with this point of view, intramolecular contribution should be minimized. Then, no major change would be expected when passing from the aminopyridines to melamine, which is in contradiction with experimental evidence.

In the present situation, we are aware that HB can contribute to the effects observed in the heterocyclic nitrogen atom qcc's in melamine but, until further experimental evidence shows it, we consider that the major contribution to the changes observed in the qcc in melamine is the intramolecular one, discussed in [4].

Conclusion

Though the results reported here do not help very much in understanding the role of hydrogen bonding in the s-triazine derivatives studied, they constitute a significant step with the observation of new lines in melamine and cyanuric chloride; also worthy of notice is the observation of positive temperature coefficients of the NQR frequencies of some lines in compounds in which hydrogen bonding is likely to occur, namely, caynuric acid and melamine. It is hoped that further investigation will lead to a deeper understanding of this interesting series of compounds in the future.

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