BROMINE NUCLEAR QUADRUPOLE RESONANCE OF CYCLOPHOSPHAZENE DERIVATIVES

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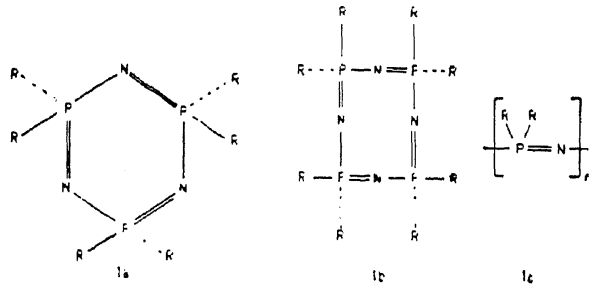
PHOSPHAZENES are cyclic or linear molecules containing alternate P and N atoms in their skeleton, having two substituents attached to the phosphorus and none to the nitrogen as shown in the figure (R = Cl, F, Br, OR, NRR′, etc.).

The potential utility of phosphazene derivatives as flame retardants for textile fibres, chemosterilant insecticides and ultrahigh-capacity fertilizers has been demonstrated[1]. There is also a growing interest in the development of organophosphazene polymers for specific applications[2].

The use of nuclear quadrupole resonance spectroscopy in the study of the structural details of phosphazenes has aroused considerable interest in recent years[3–5]. We report here the first observation of Bromine NQR in cyclophosphazenes. The compounds studied are the octabromo derivative, $N_4P_4Br_8$, and the hexabromo derivative, $N_3P_3Br_6$ (Fig. 1, *b*, *a*). We have obtained the nqr data using a super-regenerative spectrometer (constructed locally), employing a tunable transmission line having a frequency range of 140 MHz to 380 MHz.



The nqr frequencies for the octabromo derivative are given in Table I. It can be seen that the value of 1·19 obtained for the nqr frequency ratio $\nu(^{79}Br)/\nu(^{81}Br)$ agrees well with the known value of 1·21 for the Quadrupole moment ratio $Q(^{79}Br)/Q(^{81}Br)$. Two relatively broad lines (linewidth ~ 35 kHz) are observed which could be due to two inequivalent Br sites. The number of Br atoms occupying each site is likely to be the same, as is indicated by the equal intensity of the lines (S/N ~ 6 on the oscilloscope). This is supported by the crystal structure data of Zoer and Wagner[6]. There are two molecules in the tetragonal unit cell, occupying special 4 symmetry points. There are only two disinct P–Br bonds, differing by 0·01 Å in length. Thus the nqr spectrum unambiguously reveals the presence of two such inequivalent Br sites.

We also find that the difference in the frequencies of the two lines is actually higher at 77° K (4·025 MHz as against 2·585 MHz at 297° K) which shows that the chemical inequivalence is present all the more in the "stationary" molecule and is probably due to intermolecular effects. It may be pointed out here that the situation is just the opposite for the corresponding chlorotetramer, $N_4P_4Cl_8$, where the two chlorine nqr lines almost collapse into a single line at 77° K but remain separate at room temperature[7] :

TABLE I

The Br-NQR data for $N_4P_4Br_8$

Temp. °K	^{79}Br freq. (MHz)		^{81}Br freq. (MHz)		$\frac{\nu^{79}}{\nu^{81}}$
	Line I	Line II	Line I	Line II	
297	234·075 ±·005	236·640 ±·005	195·400 ±·005	197·805 ±·005	1·19
77	237·585 ±·005	241·605 ±·005	..	..	

In $N_3P_3Br_6$, where one could expect a four-line spectrum on the basis of the crystal structure data, we have obtained two lines of unequal intensity (3 : 1) at 241·5 MHz and 242·9 MHz and a broad unresolved

spectrum in the range 235 to 235·9 MHz which may be due to the overlap of the other two lines. The measurements have all been made at 77° K, using lock-in detection. Further investigations to resolve the details of this spectrum are under way.

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ULTRASTRUCTURAL STUDY ON THE FATE OF SOME SPECIAL CYTOPLASMIC INCLUSION IN PATHOGENIC *NAEGLERIA AEROBIA* (SINGH & DAS, 1970)

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ABSTRACT

Naegleria aerobia Singh and Das[1] cause primary amoebic meningo-encephalitis in man and animals. The morphological changes at the ultrastructural level associated with *N. aerobia* growing in mouse brain and on its subsequent *in vitro* culture have been reported. The major differences include the staining characteristics of mitochondria under these conditions and the appearance and disappearance of some special inclusions (black bodies) observed in the cytoplasm of these amoebae during growth *in vitro*. That the rough endoplasmic reticulum plays an important role in the gradual digestion of the black bodies has been noticed and demonstrated in the figures. The nature of these bodies and their role are discussed.

INTRODUCTION

NUMEROUS membrane bound special inclusions, observed as black bodies, in the cytoplasm of *N. aerobia* from freshly isolated infected mouse brain tissue or from infected human cases have been reported[2-6]. These bodies have not been reported in amoebae maintained in stock and used for infecting mice or in amoebae cultured from infected mouse brain and passaged through repeated subcultures *in vitro*. This communication deals with the fate of these black bodies during prolonged cultivation of the amoebae *in vitro* from brain tissues.

MATERIALS AND METHODS

The methods for culturing *N. aerobia* and infecting mice were carried out in a manner similar to those described by Das, 1977; Maitra, *et al.*[1,2]). A small portion of brain from sick mice was teased in a small quantity of distilled water (37° C) and a hanging drop preparation was made to demonstrate the amoebae. Large number of petri dishes were then smeared with *Escherichia coli* and seeded with the infected brain material. Subculture of these plates was made at every 24 h intervals. The amoebae were fixed for electron microscopy in a manner described below. The areas on a plate showing heavy bacterial growth and the pieces of brain tissue was scraped off and the plates were flooded with fixative containing 5% glutaraldehyde in 0·1M cacodylate buffer with 1 mM calcium chloride (pH 6·8). The amoebae which were on the margins of the streak were scraped and collected in centrifuge tubes, washed once by centrifugation (500 rpm) for 5 min and the sediment resuspended in fresh fixative for 5 h and the samples were centrifuged at 5000 rpm for 10 min to get a pallet. They were then washed 6–8 times during a period of 8–12 h in 0·1 M cacodylate buffer with 4·5% sucrose (pH 6·8) and fixed in Caulfield's[8] 1% osmium tetroxide at 4° C for 2 h. The amoebae were washed once in distilled water and kept in fresh 1% aqueous uranyl acetate overnight. The tissue was then dehydrated in graded alcohol or acetone and embedded in epon-araldite mixture (Mollenhouer[9]). Brains of mice showing symptoms after *N. aerobia* infection were fixed by intracerebral inoculation of fixative, the brain removed and processed in the manner described above. Silver sections were cut on LKB-Ultrotome III using a glass knife. Sections were mounted on copper grids