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Vibrational spectroscopic study on polycationic phosphorus dendrimers

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ABSTRACT

Three generations of phosphorus dendrimers with pyrrolidine end groups were synthesized for use in biology and medicine. Neutral samples are soluble in organic solvents but after protonation these dendrimers become water-soluble and can be used for biological experiments. The FTIR and FT Raman spectra of three generations of dendrimers G_i constructed from the cyclotriphosphazene core, repeating units —**O**—**C$_6$H$_4$**—**CH**=**N**—**N(CH$_3$)**—**P(S)**< and aminoethylpyrrolidine end groups —**NH**—**(CH$_2$)$_2$C$_4$NH$_9$** were registered. Analysis of the IR spectra of G_i shows that the NH groups form a hydrogen bond with chlorine atoms. The calculation of the vibrational spectra was performed for the optimal structure of the first generation dendrimer in the framework of the DFT method. The first-generation dendrimer molecule has flat, repeating units and a plane of symmetry passing through the cyclotriphosphazene core. Calculation of the distribution of the potential energy made it possible to assign the bands in the experimental vibrational spectra. Amine groups show NH stretching bands at 3397 and 3200 cm^{-1}, NH$^+$ stretching bands occur at 2645 and 2546 cm^{-1} in the IR spectrum of G_1. The stretching vibrations of the NH$^+$ group are significantly shifted to low frequencies due to the formation of a hydrogen bond with the chlorine atom. The line at 1577 cm^{-1} in the Raman spectrum is characteristic of repeating units.

1. Introduction

Owing to the strictly defined structure of dendrimers and their numerous functional groups, they have found wide applications in biology and medicine [1–5]. In particular dendrimers are more preferable for drug delivery than conventional polymers. Interaction of dendrimers with DNA makes them suitable for transfection experiments. It was shown that phosphorus dendrimers are biocompatible and are active anti-prion agents, anti-viral agents, capable of stimulating blood cells of natural killers, depending on the type of terminal groups [5]. Pyrrolidine and its derivatives are widely used in pharmacology and their introduction into the terminal groups of phosphorus dendrimers seems very promising [6–9]. After protonation of such dendrimers, their end groups become positively charged and are water- soluble. They are sensitive biosensors [5]. Polycationic dendrimers interact with DNA and are used as drugs [5]. Modified phosphorus dendrimers control the growth of cells [5]. IR spectroscopy is generally used for analytical purposes to monitor the course of the reaction, determine the type of end groups and intermolecular interactions [10–17].

In this article we report on the synthesis and study of the vibrational spectra of three generations of phosphorus-containing dendrimers constructed from the cyclotriphosphazene core, repeating units —**O**—**C$_6$H$_4$**—**CH**=**N**—**N(CH$_3$)**—**P(S)**< with aminoethylpyrrolidine end groups —**NH**—**(CH$_2$)$_2$**—**C$_4$NH$_9$** (Fig. 1). Such dendrimers have been selected because they are water soluble, have increased biological activity and are non toxic. Synthesized dendrimers have valuable biological properties and promising drugs for the treatment of a number of diseases [18,19]. The structure and vibrational spectra of the first-generation dendrimer molecule calculated by the DFT method are consistent with the experimental data [17]. It was interesting to establish the localization of charges on atoms of terminal groups that significantly affect the biological activity of dendrimers. So the main purpose of this work was to obtain the characteristic spectral features of various structural parts of the dendrimers: cyclotriphosphazene core, repeating units and

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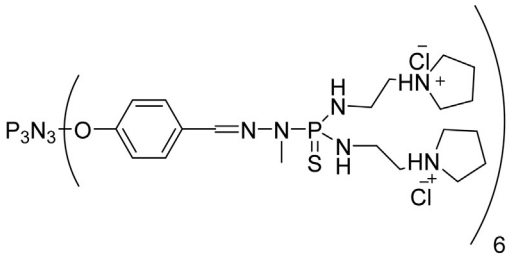

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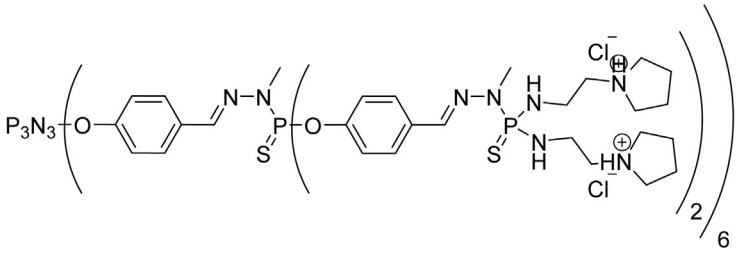

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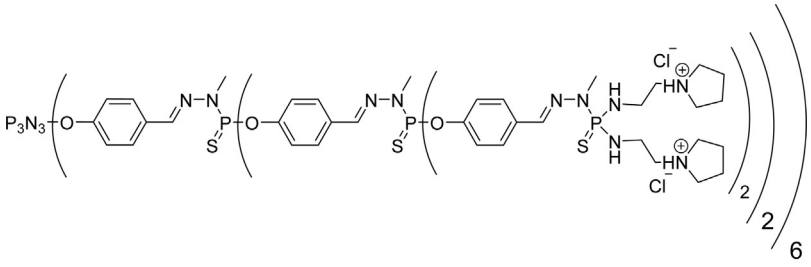

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Fig. 1. Chemical structure of the phosphorus dendrimers G_1 (1), G_2 (2) and G_3 (3).

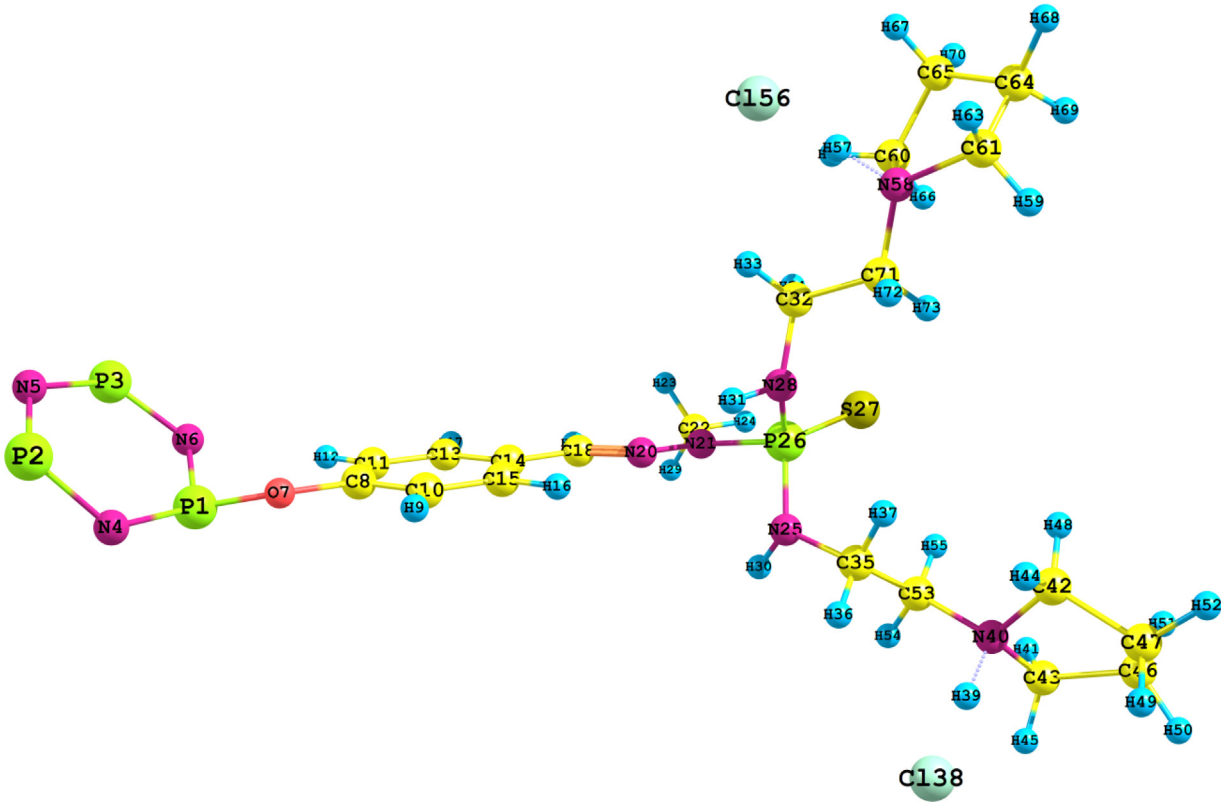

Fig. 2. Optimized geometry and atom numbering for G_1 (only one branch is shown for the clarity).