



DFT study of structure, IR and Raman spectra of the first generation dendrimer built from cyclotriphosphazene core with terminal pyrazine groups



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ABSTRACT

A phosphorus-containing dendrimer with pyrazine end groups that can be used for biological purposes has been synthesized. The vibrational spectra of the first generation dendrimer G_1 constructed from the cyclotriphosphazene core, six repeating units $-\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{N}(\text{CH}_3)-\text{P}(\text{S})<$ and twelve 4-oxyphenethylamidopyrazine end groups $-\text{O}-\text{C}_6\text{H}_4-(\text{CH}_2)_2-\text{NH}-\text{CO}-\text{C}_4\text{N}_2\text{H}_3$ were registered. Analysis of the IR spectra of G_1 shows that the amide groups form an intermolecular hydrogen bond. Optimization of the structure and analysis of normal vibrations were carried out for dendrimer G_1 using the density functional theory (DFT). The six repeating units are arranged in a symmetric manner about the cyclophosphazene ring; each side of the ring contains three repeating units. It turned out that dendrimer G_1 is a double bowl with almost flat repeating units which represent the concave surface and a core as a bottom of the bowl. The assignment of bands in the vibrational spectra was carried out by analyzing the distribution of the potential energy. Amide groups show bands at 3393, 1675 cm^{-1} in the IR spectrum of G_1 . The line at 1577 cm^{-1} in the Raman spectrum is characteristic of repeating units.

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1. Introduction

Dendrimers are highly branched monodisperse macromolecular compounds [1–3]. The shape and properties of dendrimers can be controlled [1–3]. Fragments of the dendrimer molecule: core, repeating units and end groups can be changed in a given direction [1–3].

Dendrimers are multivalent systems due to their numerous end groups [4]. Phosphorus-containing dendrimers play a specific role in interaction with biological systems from the DNA and the cells to the delivery of drugs [4]. They are a key component of nanomedicine [4]. Pyrazine and its derivatives were used to synthesize various nanomaterials based on dendrimers [5–8]. Vibrational spectroscopy makes it possible to monitor the synthesis of dendrimers to determine the type of terminal groups and the character of intra- and intermolecular interactions [9–16].

In this article we report on the investigation of the vibrational spectra together with DFT calculations of the first generation dendrimer constructed from the cyclotriphosphazene core, six repeating units $-\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{N}(\text{CH}_3)-\text{P}(\text{S})<$ with twelve 4-oxyphenethylamidopyrazine $-\text{O}-\text{C}_6\text{H}_4-(\text{CH}_2)_2-\text{NH}-\text{CO}-\text{C}_4\text{N}_2\text{H}_3$ terminal groups (Fig. 1). Such a dendrimer was chosen because a related compound with amino-bismethylene phosphonic groups can be used to activate monocytes [17]. The synthesized dendrimer has valuable biological properties and is a promising drug for the treatment of a number of diseases [18]. The calculated bond lengths of the molecule G_1 are in agreement with the experimental data [19]. So the main purpose of this work was to obtain the characteristic spectral features of various structural parts of the dendrimer: cyclotriphosphazene core, repeating units and end groups on the basis of quantum chemical calculations. The interpretation of the vibrational spectra of the dendrimer in combination with the DFT calculation is important for investigating their interactions with various guest molecules. The calculation of the spatial distribution of the electron density revealed the existence of places which in the appropriate mediums will attract ions or metal atoms. It is important to clarify how the structure of

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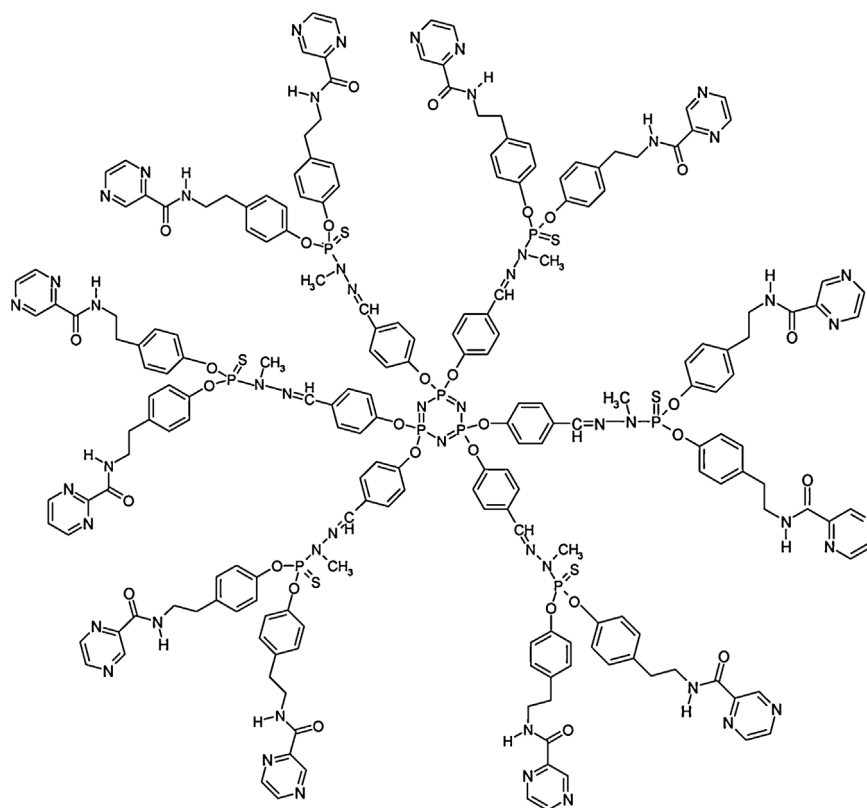


Fig. 1. Structure of dendrimer molecule G_1 .

dendrimers is manifested in their vibrational spectra. The results obtained from such an analysis contribute to an understanding of the dynamics and properties of dendrimers.

2. Experimental

The general scheme for obtaining phosphorus dendrimers has been described in sufficient details [19,20]. The most commonly used core is hexachlorocyclotriphosphazene ($N_3P_3Cl_6$). In the first stage, a dendrimer with terminal amine groups was obtained. Then the first generation dendrimer with terminal amine groups (0.1094 mmol), cesium carbonate (4.157 mmol), diisopropylamine (1.422 mmol) and phenol derivative (1.422 mmol) were stirred for 48 h in tetrahydrofuran at room temperature up to completion. After completion cesium salts were removed by centrifugation and the solvent was evaporated. The residue was extracted using dichloromethane and brine solution. The organic layer was dried over sodium sulfate and concentrated in rotary evaporator. It was further purified by column chromatography using silica as the stationary phase and methanol and chloroform (0.5:9.5) mixture as mobile phase.

The molecule G_1 consists of a cyclotriphosphazene core (NP_3), six repeating units $-O-C_6H_4-CH=N-N(CH_3)-P(S)<$, and twelve end 4-oxyphenethylamino groups $-O-C_6H_4-(CH_2)_2-NH_2$ (Fig. 1). The studied dendrimer is an amorphous solid compound.

IR spectra were recorded in the region 4000–400 cm^{-1} using Bruker Vector-22 FTIR-spectrophotometer with a resolution of 4 cm^{-1} . The samples were placed between the KBr plates. Sixty-four scans were added for each spectrum.

The Raman spectra were excited by Nd: YAG laser line 1064 nm with a power of 50 mW in the sample in the region 3500–200 cm^{-1} and recorded using RAMII with Bruker Vertex70 FT-Raman module with a resolution of 4 cm^{-1} .

3. Computational method

Since the total molecule G_1 contains 522 atoms, then for the calculation a model was chosen in which only one branch was left and five branches were replaced by methoxy groups (Fig. 2). DFT calculations were performed with the PBE density functional [21] using the TZ2P basis set [22] and the program PRIRODA [23]. For a better agreement with the experiment, the calculated wavenumbers in the range from 3500 to 2700 cm^{-1} were scaled by a factor 0.967. The numeric value for the scaling factor was obtained by minimizing the mean square deviation of calculated and experimental wavenumbers [24].

The relative intensities of the lines in the Raman spectrum were calculated from the Raman activity S_i , obtained using the program PRIRODA according to the equation: $I_i = \frac{f(v_0 - \nu_i)^4 S_i}{\nu_i [1 - \exp(-hc\nu_i/kT)]}$, where ν_0 being the exciting wavenumber in cm^{-1} , ν_i the vibrational wavenumber of i -th normal mode, h , c and k universal constants and f normalization factor.

Theoretical spectral curves were constructed using the Lorentzian band shape and half-width of bands equal to 10 cm^{-1} . The assignment of bands was performed by calculating the distribution of potential energy (PED) and using the animation option of the program GaussView 4.1 [25]. To calculate PED the software package SHRINK was used [24].

Calculations of the natural bonding orbitals (NBO) [26] for G_1 were performed using the Gaussian 09 program package [25]. The electronic chemical potential, the chemical hardness, softness, and global electrophilicity index were obtained from the expressions $\mu \approx -(IE + EA)/2$, $\eta \approx (IE - EA)$, $S = 1/\eta$, and $\omega = \mu^2/2\eta$ in terms of the first vertical ionization energy IE and electron affinity EA , respectively [27].

The Fukui functions $f_k^+(r) = [q_k(N + 1) - q_k(N)]$ for nucleophilic attack, and $f_k^-(r) = [q_k(N) - q_k(N - 1)]$ for electrophilic attack,

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