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Structure, IR and Raman spectra of phosphotrihydrazide studied by DFT

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ABSTRACT

The FTIR and FT Raman measurements of the phosphotrihydrazide $(S)P[N(Me)-NH_2]_3$ have been performed. This compound is a zero generation dendrimer G_0 with terminal amine groups. Structural optimization and normal mode analysis were obtained for G_0 by the density functional theory (DFT). Optimized geometric bond length and angles obtained by DFT show good agreement with experiment. The amine terminal groups are characterized by the well-defined bands at 3321, 3238, 1614 cm^{-1} in the experimental IR spectrum and by bands at 3327, 3241 cm^{-1} in the Raman spectrum of G_0. The experimental frequencies of asymmetric and symmetric NH_2 stretching vibrations of amine group are lower than theoretical values due to intramolecular N—H⋯S hydrogen bond. This hydrogen bond is also responsible for higher experimental infrared intensity of these bands as compared with theoretical values. Relying on DFT calculations a complete vibrational assignment is proposed for the studied dendrimer.

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1. Introduction

Dendrimers, a very interesting class of monodisperse macromolecules with a highly branched architecture that can display useful properties in various fields such as catalysis, electrochemistry, photophysics, pharmaceutical and medical applications [1–3]. Three structural components of dendrimers namely inner core, repeating units and terminal functional groups can optionally be varied [4–6]. Strict control of the size, shape, and the properties of the dendrimer can be achieved [4–6]. Three different methods for the synthesis of small phosphorus dendrimers were described [7]. These species were obtained up to the first or second generation using the phosphotrihydrazide $(S)P[N(Me)-NH_2]_3$ [7]. To better understand the structure and properties of dendrimers it is necessary to study the electronic structure of the first generations of dendrimers by methods of quantum chemistry. Synthesis and vibrational spectra of phosphorus dendrimers with thiophosphoryl core were reported [8–10].

In this article, we report on study of the vibrational spectra and DFT calculations of the phosphotrihydrazide (G_0) which is a zero generation dendrimer with a conical architecture. This work is a continuation of the spectral and quantum chemical studies of the structure and reactivity of the dendrimers [8–10]. Calculated geometrical parameters were compared with experimental data obtained by X-ray diffraction [11]. So the main purpose of this work was to obtain the spectral characteristic of different structural parts of the dendrimer: a core and terminal amine groups on the basis of quantum chemical calculation. The results will allow understanding the structure, dynamics and properties of dendrimers.

2. Experimental

Synthesis and characteristics of the investigated dendrimer were described previously [7]. The G_0 molecule comprises a core P=S and amine —NH_2 end groups (Fig. 1). The studied dendrimer is a crystalline compound.

IR spectra were recorded in the region 4000–400 cm^{-1} by using a Bruker Vector-22 FTIR-spectrophotometer with a resolution of 4 cm^{-1}. Samples for the registration of the IR spectra were prepared in KBr pellets. Sixty-four scans were added for each spectrum.

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

3. Computational method

Calculation of the IR and Raman spectra of G_0 molecules was performed using density functional theory with the B3LYP functional (DFT/B3LYP) and 6-31++G(d,p) basis set. Gaussian 09 program was used to perform DFT calculations [12]. Minima on the potential energy surface were found by relaxation of the geometrical parameters with standard methods of optimization. All stationary points were characterized as minima by the analysis of the Hessian. It is known that the harmonic vibrational frequencies calculated by DFT method are usually higher than the experimental values due to an approximate consideration
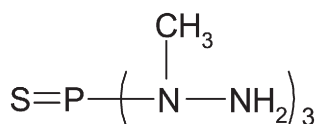
Fig. 1. Structure of dendrimer molecule G_0.

of electron correlation, shortcoming of basis sets, the effects of anharmonicity [13]. To account for these effects calculated frequencies are usually scaled. In this work for a better agreement with the experiment calculated the wave numbers were scaled by linear scaling procedure $\nu_{obs} = (1.0087 - 0.0000163\, \nu_{cal})\nu_{cal}$ [14].

The absolute Raman intensity calculated from the Raman activity S_i, obtained with Gaussian 09 program, according to the equation: $I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i[1 - \exp(-hc\nu_i/kT)]}$, 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 the normalization factor. Raman spectra were generated from the list of frequencies and intensities using Lorentzian band shape and half-width of 10 cm^{-1} for each of vibration modes. Classification of bands was performed on the basis of the calculated potential energy distribution (PED) and animation options of Gauss view 4.1 programs [12]. The SHRINK software package was used to calculate the potential energy distribution (PED) [15].

Natural bonding orbital (NBO) calculations [16] of G_0 were performed using Gaussian 09 [12] software package on the same level of theory for understanding the different types of interactions between filled orbitals of one subsystem and vacant orbitals of the other subsystems that quantify intermolecular delocalization or hyper conjugation. Fock matrix analysis using second-order perturbation theory was made to assess the donor-acceptor interactions. For each donor (i) and acceptor (j), stabilization energy E_2 associated with delocalization $i \rightarrow j$ estimated as $E_2 = \Delta E_{ij} = \frac{q_i(F_{ij})^2}{\varepsilon_j - \varepsilon_i}$ where q_i the donor orbital occupancy, ε_j and ε_i are diagonal and F_{ij} off-diagonal NBO Fock matrix elements [16].

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 [17]. 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, where q_k is the electronic population of atom k in the molecule, N the number of electrons, were calculated. The local softness is obtained by projecting the global quantity onto any atomic center k in the molecule by using the Fukui function: $s_k^+ = Sf_k^+$, $s_k^- = Sf_k^-$ The Fukui function and local

softness for each reactive atom were calculated using Natural atomic charges population analysis [16].

4. Results and discussion

The optimized structural parameters of G_0 calculated by DFT/B3LYP level with 6-31++G(d,p) basis set are listed in Table 1 in accordance with the atom numbering scheme given in Fig. 2. The studied dendrimer G_0 molecule possesses multiple conformations, the preferred ones of which are those with heteroatoms far as much as possible (Fig. 1). The experimental geometry was used as starting point of the optimization.

Geometrical parameters of G_0 in the crystalline state were defined by the X-ray diffraction [11]. This compound has achiral molecules and possesses C_3 symmetry. The crystal structure of G_0 reveals that it self-assembles into a 3-D tubular structure that is facilitated by the N—H⋯S hydrogen bonds [11]. Each of three $N(CH_3)NH_2$ substituents attached to the phosphorus center in G_0 acts as a proton donor (NH) while the S atoms of the three neighboring molecules act as proton acceptors [11]. There are no differences among the chemically equivalent bond lengths.

The structure of G_0 molecule is defined by the dihedral angles SPNN and SPNC which determine the orientation of the branches and terminal groups. Although the comparison between the structures in the gas and condensed phases is not direct, we can observe a reasonable agreement between the theoretical calculations and the experimental X-ray diffraction data for the crystalline phase of G_0 [11] (Fig. 2, Table 1). Calculated bond lengths (in Å) 1.960 (P(1)–S(2)), 1.704 (P(1)–N(4)), 1.425 (N(3)–N(4)), 1.463 (C(5)–N(4)) are in good agreement with the experimental values 1.958, 1.661, 1.429, 1.462. Theoretical bond angles (in degrees) S(2)–P(1)–N(4) (112.9), P(1)–N(4)–N(3) (115.2), P(1)–N(4)–C(5) (120.0) are also in close agreement with the experimental values 111.5, 113.2, 120.3.

The bonding between the phosphorus and nitrogen atoms is described in terms of σ bonding and additional π bonding arising from the overlap of $3d$ orbitals of the phosphorus with nitrogen p orbitals [18]. The experimental P(1)–N(4) bond length of 1.660 in G_0 are shorter than so-called single P—**N** bond 1.77 Å.

The dendrimers shape can be characterized by ratios I_1/I_3 and I_2/I_3 of the principal moments of gyration tensor. The difference of these ratios from 1 characterizes the deviation of dendrimers shape from the sphere. For the studied dendrimer the calculated values of I_1/I_3 and I_2/I_3 of the principal moments of gyration tensor are 0.89 and 0.98. Thus the G_0 molecule has a slightly asymmetric shape. The shape of dendrimer molecules defines their capability to self-assembling or self-ordering in various hierarchical structures.

Table 1
Experimental and calculated bond distances (Å) and bond angles (°) of G_0 calculated at DFT/B3LYP/6-31++G(d,p) level.

Experimental [11]	alc.		Experimental [11]	alc.	
Bond distances					
P(1)–S(2)	1.958	1.960	N(11)–N(12)	1.429	1.424
P(1)–N(4)	1.661	1.704	N(19)–N(20)	1.429	1.424
P(1)–N(12)	1.660	1.704	C(5)–N(4)	1.462	1.463
P(1)–N(20)	1.660	1.704	C(13)–N(12)	1.462	1.463
N(3)–N(4)	1.429	1.425	C(21)–N(20)	1.462	1.463
Angles					
S(2)–P(1)–N(4)	11.5	12.9	P(1)–N(20)–N(19)	13.2	15.1
S(2)–P(1)–N(12)	11.5	12.9	P(1)–N(4)–C(5)	20.3	20.0
S(2)–P(1)–N(20)	11.5	13.0	P(1)–N(12)–C(13)	20.4	19.9
P(1)–N(4)–N(3)	13.2	15.2	P(1)–N(20)–C(21)	20.4	19.8
P(1)–N(12)–N(11)	13.2	15.2			
Dihedral angles					
S(2)–P(1)–N(4)–N(3)	56.5	59.3	S(2)–P(1)–N(4)–C(5)	−60.2	−55.2
S(2)–P(1)–N(12)–N(11)	56.5	58.9	S(2)–P(1)–N(12)–C(13)	−60.2	−55.6
S(2)–P(1)–N(20)–N(19)	56.5	159.1	S(2)–P(1)–N(20)–C(21)	−60.2	−55.4