

DFT analysis of structure and IR spectra of phosphorus G_{1V} generation dendron

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Abstract

FT-IR spectra of phosphorus dendron G_{1V} generation with terminal P-Cl groups have been recorded. Density functional theory is used for analyzing the properties of each structural part (core, branches, surface). It is found that the repeating branching units of G_{1V} exist in a single stable conformation with planar $-\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{N}(\text{CH}_3)-\text{P}$ fragments. DFT results for the structure of G_{1V} are in good agreement with recent X-ray diffraction measurements. A complete vibrational assignment is proposed for different parts of G_{1V} . The global and local reactivity descriptors have been used to characterize the reactivity pattern of the core function and terminal group. Our study reveals that the most reactive site of G_{1V} is the core function and $=\text{CH}_2$ side of vinyl group is preferred for nucleophilic attack. In the dendrimer G_1 the most reactive are the terminal groups. IR spectroscopy combined with ab initio DFT computation provides unique detailed information about the structure and reactivity of the technologically relevant materials, which could not be obtained before with any other technique.

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1. Introduction

Dendritic-type architectures are frequently encountered in the biological world, such as the branches and roots of plants [1–3]. Dendrimers constitute a small-scale artificial model of these natural dendritic architectures [4–6]. The three structural components of dendrimers, namely an interior core, repeating branching units radially attached to the core, and functional terminal groups attached to the outermost branching units, can be tuned at will [2]. A fine control of the overall size (the generation), shape, and properties of the dendrimer, creating special three-dimensional environments, can be achieved [2]. To yield a better understanding of the properties imparted by each component to the whole structure and the influence of each part on the others, it is highly desirable to introduce the quantum density functional theory (DFT) studies of electronic structure of low-generation dendrimers.

The preparation and IR and Raman spectra of phosphorus dendrimers built up to 12th generation with terminal aldehyde and P-Cl groups were reported [7–13]. Considering the size of dendrimer molecules the difficulty arises in spectral interpretation, and, therefore, DFT calculations would help facilitate spectral assignment.

In this work, our aim is to combine the experimental results with ab initio quantum chemical DFT calculations to interpret IR spectra of the phosphorus first generation dendron with terminal P-Cl groups (G_{1V}). During full DFT optimization we were able to find the local minimum conformer of G_{1V} and its IR spectra. The values of calculated geometric parameters were compared with precise molecular structure derived by the X-ray analysis [7]. Thus, the main aim of this work was to obtain the characteristic spectral features of structural parts of dendrimers: the core function, the repeated units and the terminal P-Cl groups. A detailed analysis of the IR spectra for the lowest energy conformer of G_{1V} is important for investigation of supramolecular properties of phosphorus dendrimers as containers for different guest molecules. It enables to determine the active sites of the dendrimer molecules for nucleophilic and electrophilic attack. The calculated electronic density spatial distribution reveals the existence of regions where

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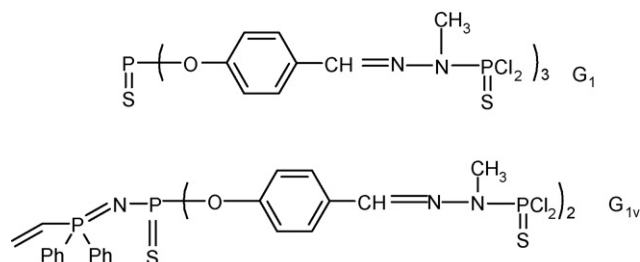


Fig. 1. The structure of dendron G_{1v} and dendrimer G_1 .

appropriate environments would attract either an ion or a metal atom.

The global and local reactivity descriptors have been used to characterize the reactivity pattern of the core function and the terminal groups. The results that emerge from such an analysis contribute to the understanding of the structure, dynamics and properties of dendrimers.

2. Experimental

The synthesis and main characteristics of the studied phosphorus dendron and dendrimer were described earlier [7,8]. The G_1 molecule contains the following parts: the trifunctional core (C) $S=P(-O-)_3$, the bifunctional repeating unit (R) $-O-C_6H_4-CH=N-N(CH_3)-P(S)<$ and the Cl atoms as the terminal groups (T) (Fig. 1). The corresponding dendron G_{1v} instead of one repeated unit with two terminal groups has the $H_2C=C-P(Ph)_2=N-$ unit (A) attached to phosphorus atom (Fig. 1).

IR spectra in the region $3500\text{--}400\text{ cm}^{-1}$ were recorded on a Vector-22 Bruker FT-IR spectrophotometer with a 4 cm^{-1} resolution.

3. Computational method

Calculations of IR spectra of the dendron G_{1v} were carried out using the gradient-correlated density functional theory with Perdew–Burke–Ernzerhof exchange–correlation functional (DFT/PBE) [14]. This functional is very satisfactory from the theoretical point of view, because it verifies many of the exact conditions for the exchange–correlation hole and it does not contain any fitting parameters [15]. The binding energies, geometries and dynamical properties of different molecules calculated with PBE functional show the best agreement with experiment [16,17]. Calculations were performed using three exponential basis with two polarizing functions (TZ2P) [18]. This basis set was chosen in order to obtain the most advantageous relation of accuracy and computation time [18]. Its peculiarity is that the same set of exponents is used for all values of angle moment in atom [18]. The program PRIRODA was used to perform DFT calculations [18]. All stationary points were characterized as minima by analysis of Hessian matrices. The software package SHRINK was used for the transformation of quantum mechanical Cartesian force constants to the matrix in redundant internal coordinates and calculation of potential energy distribution [19]. No scaling procedure of frequencies or force constant

was applied. Recently, we checked the selected functional and basis set by calculation of geometry and IR spectra of dendrimers [20–22].

The minima of the potential surface were found by relaxing the geometric parameters with standard optimization methods. IR spectra were generated from a list of frequencies and intensities using Gaussian band shape and half-width σ of 5 cm^{-1} for each of N vibration modes calculated. The intensity of each band is A_k in km/mol .

$$I(\nu) = \sum_k^N \frac{A_k}{\sqrt{2\pi\sigma}} \exp\left\{-\frac{(\nu - \nu_0)^2}{2\sigma^2}\right\}$$

An assignment of bands was fulfilled on the basis of calculated potential energy distribution (PED).

The electronic chemical potential, the chemical hardness and softness were obtained from the expressions $\mu \approx -(IE + EA)/2$, $\eta \approx (IE - EA)$ and $S = 1/2\eta$, in terms of the first vertical ionization energy IE and electron affinity EA , respectively [23]. 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 centre k in the molecule by using the Fukui function: $s_k^+ = S f_k^+$, $s_k^- = S f_k^-$. The Fukui function and local softness for each reactive atom were calculated using Hirshfeld population analysis [24].

4. Results and discussion

An X-ray diffraction study of dendrimer G_1 was undertaken in order to understand why it is possible to obtain such large phosphorus macromolecules [9]. Three main features of this compound can be emphasized. Each $-O-C_6H_4-CH=N-N(CH_3)-P$ arm is planar. The molecule G_1 as a whole looks like a three blade propeller when examined in the direction of terminal P=S groups. The distance between terminal P=S groups is very large (17 \AA). The length of each arm is 9 \AA [9].

An X-ray structure analysis of compound G_{1v} reveals that each $OC_6H_4CH=N-N(CH_3)P=S$ arm is flat, a tendency which was already seen for other small dendrimers possessing this linkage [7,8].

DFT optimization for G_{1v} gave planar conformation of the repeated units (the Cartesian coordinates for all atoms are included in supplementary material). The planar structure of the repeating units is maintained, because the gain in steric strain, when this fragment is twisted about the single bonds, is not enough to offset the loss in conjugation energy, as a consequence of decreased π -overlap.

The structure of G_{1v} molecule is defined by the dihedral angles SPOC, POCC and SPNP, which determine the orientation of the repeating units and the core function. Full optimization yielded a single stable conformation of G_{1v} with dihedral angles ($^\circ$) 49.0 and 58.3 (SPOC), 97.1 and 89.9 (POCC), 27.5 (SPNP) in qualitative agreement with experiment 38.9, 48.9, 82.4, 65.2, 1.0

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