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Comparative DFT study of structure, reactivity and IR spectra of phosphorus-containing dendrons with P=N—P=S linkages, vinyl and azide functional groups

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HIGHLIGHTS

- FT IR and Raman spectra of the phosphorus dendrons were studied.
- The vibrational analysis was performed.
- The reactivity of dendrons was characterized.

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ABSTRACT

Fourier transform IR spectra of the first generation dendrons built from thiophosphoryl core with terminal P—Cl groups, vinyl (G_1) and azide (G_2) functional group at the level of the core have been recorded. The optimized geometries of low energy isomers of G_1 and G_2 have been calculated by density functional (DFT) method at the PBE/TZ2P level of theory. DFT is used for analyzing the properties of each structural part (core, branches, surface). It was found that the repeated branching units of G_1 and G_2 contain planar $\mathbf{-O-C_6H_4-CH{=}N-N(CH_3)-P}\!<$ fragments. DFT results for the structure of G_1 and G_2 are in good agreement with X-ray diffraction measurements. A complete vibrational assignment is proposed for different parts of G_1 and G_2. The global and local reactivity descriptors have been used to characterize the reactivity pattern of the core functional and terminal groups. Natural bond orbital (NBO) analysis has been applied to comparative study of charge delocalization. Our study reveals why azide group linked to phosphorus has a different reactivity when compared to organic azides.

Introduction

Dendritic macromolecules are highly branched compounds having well defined three-dimensional size, topology and functionalities [1–3]. The three structural components of dendrimers, namely an interior core, repeated branching units radially attached to the core, and functional terminal groups attached to the outermost branching units, can be tuned at will [4–6]. The dendrons possess functional groups on the surface and another single one reactive functional group at the level of the core [1]. The grafting of dendrons on dendrimers allows to increase the number of end groups of the dendrimer in one step [1]. The chemical diversity of the functional groups located at the core, its reactivity and its compatibility with the functional groups located on the surface remains an interesting problem. The use of divergent strategies is a fruitful approach for the synthesis of phosphorus-containing dendrons [6,7]. Different synthetic processes have been devised, depending on the type of functional group located at the core [6,7].

The first type of functional group at the core of a dendron was alkenes, due to the wide range of reactions that could be carried out later with these functional groups [6,7]. This dendron possesses a vinyl group activated by a P=N—P=S linkage at the core [6,7].

The second type of functional group that we intended to introduce at the core of dendrons was azide derivatives [6,7]. Organic azides are employed in chemistry, biology, medicine, and materials science [8]. Besides organic azides, in which the azide function is connected directly to carbon atom, hetero azides are of importance

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in organic synthesis [8]. An azide linked to a phosphorus seems to have a different reactivity when compared to organic azides: we cannot perform Huisgens (click) reaction with alkynes [8]. However, we can perform Staudinger reactions with phosphines [8]. Several phosphorus azides were used for the synthesis of various types of dendrimers, dendrons and hyperbranched polymers [6,7]. A Staudinger reaction between a phosphine and an azide linked to a P(S) group creates a phosphazene linkages substituted by a thiophosphoryl group (P=N—P=S) [6,7]. This linkage is particularly interesting for further reactions at specific layers within the structure of a dendrimer [6,7].

Phosphazenes are a class of chemical compounds in which a phosphorus atom is covalently linked to a nitrogen atom by a double bond and to three other atoms or radicals by single bonds [8]. Synthesis, reactivity, properties and applications of dendrimers built from cyclotriphosphazene core was described [4]. The reactivity at the core of most of dendrons that we have synthesized is related to the presence of a **P=N—P=S** group. In addition to its own reactivity this group may also enhance the reactivity of other functional group linked to it. The **P=N—P=S** linkage has a high electron density on sulfur which allows the regiospecific complexation of gold, whereas the other **P=S** groups do not react this way. This allows the reaction of the **P=N—P=S** linkage with electrophiles such as methyl triflate [6,7]. The **P=N—P=S** linkage also induces an electron-withdrawing effect on the functional group linked to the phosphazene, which we exploited particularly when a vinyl group is linked to this phosphorus [6,7]. The alkylated **P=N—P=S** core of dendron was used for building special architectures [6,7].

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-chemical density functional theory (DFT) studies of electronic structure of low-generation dendrimers. The preparation, IR and Raman spectra of phosphorus dendrimers built up to 12th generation with terminal aldehyde and P—Cl groups were reported [9–14]. 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 quantum-chemical DFT calculations to interpret IR spectra of the first generation phosphorus-containing dendrons possessing vinyl (G_1) and azide (G_2) functional group at the level of the core and 4 chlorines on the surface. During full DFT optimization we were able to find the low-energy conformers of G_1, G_2 and their IR spectra. The values of calculated geometric parameters were compared with precise molecular structure derived by the X-ray analysis [5,9,10]. Thus, the main aim of this work was to obtain the characteristic spectral features of structural parts of dendrons: the core function, the repeated units and the terminal *P—Cl* groups. A detailed analysis of the IR spectra of G_1 and G_2 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 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 of dendrons G_1 and G_2. Natural bond orbital (NBO) analysis of the G_1 and G_2 molecules has been applied to comparative study of charge delocalization in the $\mathbf{N_3{-}P}$, **C=C**, and **P=N—P=S** groups. The results that emerge from such an analysis contribute to the understanding of the structure, dynamics and properties of dendrimers.

Experimental

The synthesis and main characteristics of the studied phosphorus dendrons were described earlier [5–7]. The G_2 molecule contains the following parts: the trifunctional core $\mathbf{S{=}P{-}({-}O{-})_3}$, the bifunctional repeated units $\mathbf{{-}O{-}C_6H_4{-}CH{=}N{-}N(CH_3){-}P(S)}{<}$, the **Cl** atoms as the terminal groups, and the **N=N—N—** unit attached to phosphorus atom (Fig. 1). The corresponding dendron G_1 instead of azide group has the $\mathbf{H_2C{=}C{-}P(Ph_2){=}N{-}}$ unit attached to phosphorus atom (Fig. 1). The dendrons G_1 and G_2 were obtained as white powder.

IR spectra in the region 4000–400 cm^{-1} have been recorded with a Vector-22 Bruker FTIR-spectrometer. The spectral resolution was set at 4 cm^{-1}. Sixty-four scans were added for each spectrum. The powder samples were studied in KBr pellets.

Computational method

Calculations of IR and Raman spectra of the dendrons G_1 and G_2 were carried out using the gradient-correlated density functional theory with Perdew–Burke–Ernzerhof exchange-correlation functional (DFT/PBE) [15]. This functional is very satisfactory from the theoretical point of view, because it does not contain any fitting parameters [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. Its peculiarity is that the same set of exponents is used for all values of angle moment in atom. The program PRIRODA was used to perform DFT calculations [19]. The minima of the potential surface were found by relaxing the geometric parameters with standard optimization methods. All stationary points were characterized as minima by analysis of Hessian matrices. All electronic energies were corrected for the zero point vibrational energy. The theoretically obtained structural and spectroscopic data reported in this article are for the energetically preferred conformers at 298 K, 1 atm. The software package SHRINK was used for the transformation of quantum mechanical Cartesian force constants to the matrix in a redundant set of internal coordinates and calculation of potential energy distribution [20]. For PBE with TZ2P basis set, the wavenumbers in the range from 3600 to 2000 cm^{-1} are scaled with 0.977. The other wavenumbers remain unscaled. The selected functional and basis set was checked by calculation of geometry and IR spectra of dendrimers [21,22].

Spectra were generated from a list of frequencies and intensities using Lorentzian line shape and width at half-height of 10 cm^{-1} for each of vibrational modes calculated was chosen in accordance with experimental data. An assignment of bands was fulfilled on the basis of calculated potential energy distribution (PED).

The natural bonding orbital (NBO) calculations [23] of G_1 and G_2 were accomplished using Gaussian 09 [24] package at the same level of theory in order to comprehend various second order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which quantify the intermolecular delocalization or hyper conjugation. The second order perturbation theory analysis of Fock matrix in NBO basis of G_1 and G_2 was carried out to evaluate the donor–acceptor interactions. For each donor (i) and acceptor (j), the stabilization energy E_2 associated with the delocalization $i \to j$ is estimated as $E_2 = \Delta E_{ij} = \frac{q_i (F_{ij})^2}{\varepsilon_j - \varepsilon_i}$ where q_i is the donor orbital occupancy, ε_j and ε_i are diagonal elements and F_{ij} is the off diagonal NBO Fock matrix element [23].

The electronic chemical potential, the chemical hardness, softness, and global electrophilicity index were obtained from the