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Vibrational spectra study of phosphorus dendrimer containing azobenzene units on the surface

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HIGHLIGHTS

- The FTIR and FT Raman spectra of the phosphorus dendrimers were studied.
- The structural optimization and normal mode analysis were performed for dendrimer.
- Dendrimer molecule has a concave lens structure.
- The frequencies of vibrations for the *E*- and *Z*-forms were calculated.

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ABSTRACT

The FTIR and FT Raman spectra of the first generation dendrimers, possessing oxybenzaldehyde (G_1) or oxyphenylazobenzaldehyde (G_2) terminal groups and sodium 4-[4-oxyphenyl)azo]-benzaldehyde (*SOAB*) were studied. The structural optimization and normal mode analysis were performed for dendrimer G_2 on the basis of the density functional theory (DFT). These calculations gave the frequencies of vibrations, infrared intensities and Raman scattering activities for the *E*- and *Z*-forms of azobenzene unit. The energy differences between the *E*- and *Z*-forms are 12.62 and 25.16 kcal/mol for *SOAB* and G_2. The calculated in gas phase dipole moments for the *E*- and *Z*-forms are equal to 20.86, 18.28 D (*SOAB*) and 7.56, 8.88 D (G_2). The calculated geometrical parameters and harmonic vibrational frequencies are predicted in a good agreement with the experimental data. It was found that dendrimer G_2 molecule has a concave lens structure with planar —O—C_6H_4—CH=N—N(CH_3)P=S and —O—C_6H_4—N=N—C_6H_4—CH=O fragments and slightly non-planar cyclotriphosphazene core. The experimental IR and Raman spectra of dendrimer G_2 were interpreted by means of potential energy distributions. Relying on DFT calculations a complete vibrational assignment is proposed. The strong band 1598 cm^{-1} in the IR spectra show marked changes of the optical density in dependence of substituents in the aromatic ring. The differences in the IR and Raman spectra of *SOAB* and G_2 for the *E*- and *Z*-forms of azobenzene units were cleared up. During structural isomerization of azobenzene units, redistribution of band intensities appears to a much higher extent than frequency shifts.

1. Introduction

Due to the numerous potential applications, in the fields of catalysis, materials, biology and medicine, dendrimers constitute an important class of macromolecular compounds, [1–3]. Dendrimers are built step by step, by the repetition of a sequence of reactions, which allow multiplying the number of branches and the number of end groups. The number of peripheral units and the global shape are closely related to the nature of the core; molecule has mainly a three-dimensional tree-like structure, emanating from one center – the core, with branches (dendrons). The size of such a molecule is determined by the generation number, i.e. by the length of the dendrons, which consist of an equal number of repeating units terminated by the end groups. Dendrimers have a tree-like three dimensional structure with exact numbers of repeating units and terminal groups, i.e. they are monodisperse compounds, thanks to their step-by-step synthesis.

Azobenzene groups have already been included through-out the dendritic architecture [4,5] and were used to study the encapsulation of guest molecules [6], optical switching [4], holographic storage [7], light harvesting [5], and nonlinear optical materials [8]. The design of new dendritic structures having azobenzene derivatives precisely placed at some generations in the interior and on

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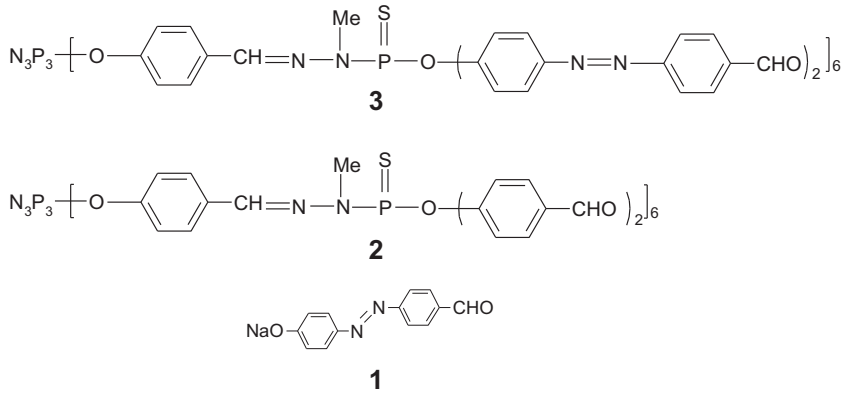

Fig. 1. Structure of model compound *SOAB* (1) and dendrimers G_1 (2) and G_2 (3).

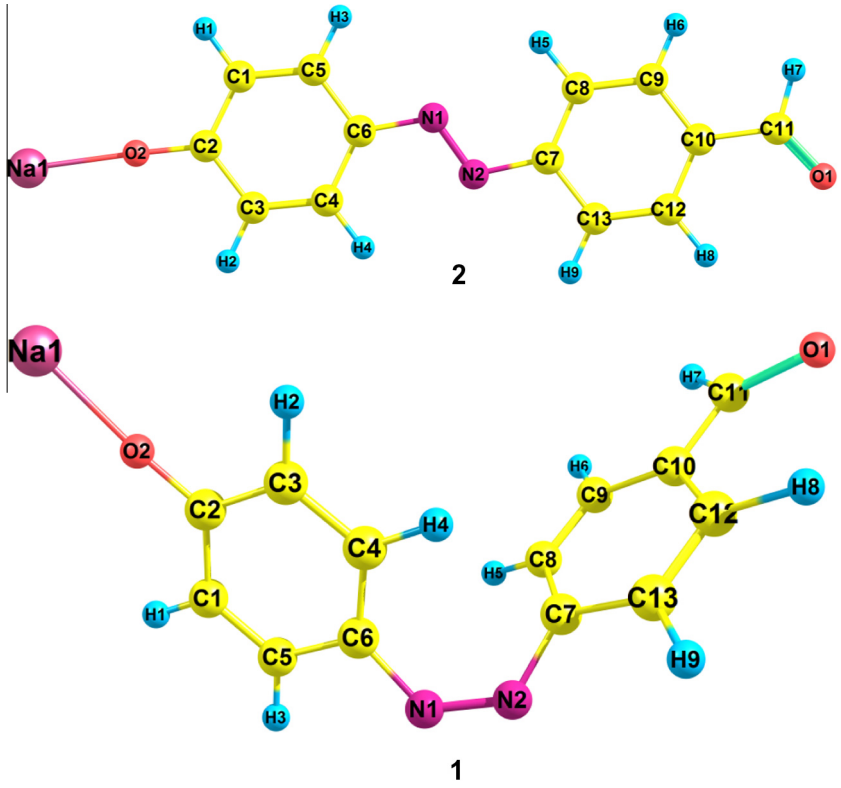

Fig. 2. Optimized geometry and atom numbering of *Z*- (1) and *E*-forms (2) of *SOAB*.

the surface were described [9]. Irradiation at 350 nm induces isomerization of the azobenzene groups from the *E* form to the *Z* form, whatever their location [9]. The thermal back-isomerization to the *E* form in the dark at room temperature was observed [9].

The techniques used for characterizing such macromolecular compounds should afford not only their chemical composition but also their morphology, shape and homogeneity. NMR spectrometry [10], UV–VIS spectrometry [9] was used to study the kinetics of $Z \rightarrow E$ back-isomerization, but FTIR spectroscopy should afford additional information [11].

In this work FTIR and FT-Raman spectroscopy were used for characterization of the dendrimers, built from the cyclotriphosphazene core, with oxybenzaldehyde (G_1) and oxyphenylazobenzaldehyde (G_2) terminal groups. The model compound with azobenzene unit sodium 4-[4-oxyphenyl)azo]-benzaldehyde (*SOAB*) was also studied. We choose azobenzene groups as the photoactive moiety since it is well known that they undergo the efficient and fully reversible photoisomerization reaction [12]. Our aim was to combine the experimental results with density functional theory (DFT) quantum chemical calculations to interpret IR and Raman spectra of dendrimer with azobenzene units. During full optimization we were able to find local minimums of the *E*- and *Z*-forms of G_2 and their IR and Raman spectra using DFT techniques. We have obtained structural parameters for dendrimer G_2 and compared them to the experimental values. Thus the main aim of this work was to characterize the structural forms of dendrimer G_2 based on IR and Raman spectra study and DFT analysis. The results that emerge from such an analysis contribute to the understanding of the structure, dynamics and properties of dendrimers.

2. Experimental

Synthesis and main characteristics of dendrimers G_1 and G_2 were described earlier [9,13] (Fig. 1). The molecules built of