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Synthesis and Comparative Characteristic of Organophosphorus Dendrimers with Phenoxy and Deuterophenoxy End Groups

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Abstract—Two series of generation 0 to 6 phosphorus dendrimers (6 to 384 end groups) are synthesized starting from the cyclotriphosphazene core. The series are distinguished by the type of their terminal groups: O–C_6H_5 in first series and O–C_6D_5 in the other. These functions are chemically analogous, but they give different spectroscopic signatures which afford detailed information about the structure of these dendrimers.

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INTRODUCTION

Dendrimers are nanomolecules synthesized from monomers that combine with each other to form a tree-like structure [1]. The growth begins with a core, viz. a polyfunctional center. The name of these compounds completely reflects their structure; it was introduced by Tomalia et al. [2] and originates from two Greek roots: “dendron” (tree) and “meros” (part). The tree-like structure is formed by a repetition of one and the same reaction sequence to give, at the end of each cycle, one new generation and identically growing number of branches. After several generations, the dendrimer gets highly branched, polyfunctional, and, as a rule, spherically shaped. Due to the presence of a great number of end groups, many branches form internal cavities coming down to the core.

A dendrimer consists of three different parts:

(1) a core: an atom or a group having at least two indentical reaction centers;

(2) branches of repetitive units radiating from the core and having at least one branching point; the units built up by an exponential law, forming concentric layers called generations;

(3) various functional end groups which are mostly localized at the dendrimer periphery (surface) and contribute much into the properties of these nanomolecules.

Dendrimers are also isomolecular polyfunctional polymers with quite specific solubilities, viscosities, and thermal stabilities. Their application field is extending from year to year and includes molecular and supramolecular chemistry, catalysis, basic research, nanotechnologies, sensors, and materials for photonics, biology, diagnostics, medicine, etc. Such extensive applications are due to the fact that dendrimers exhibit properties of polymers: Their functional groups are readily accessible on the surface and available for controlled modification; these molecules feature porosity, flexibility of inner branches, accessibility of the core, etc. Most industries make use of this new class of special polymers [3].

Research on dendrimers contributes into the understanding the behavior of such nanomolecules not only from the reactivity but also from the physicochemical standpoints. Studying physicochemical properties of dendrimers is not a trivial task, since one has to know, along with the chemical composition and uniformity, molecular morphology and shape. The dendrimer science is at the interface between molecular and polymer chemistry. Dendrimers are obtained by step-by-step controlled synthesis, but they also pertain to polymers due to their their repetitive structure made of monomers. A priory they benefit from analytical techniques applied in organic synthesis and polymer chemistry.

Since 1994 the French National Center for Scientific Research has been involved in research on synthesis, properties, and practical application of dendrimers containing one phosphorus atom in each divergence point and –CHO or $–P–(S)Cl_2$ as end groups [4]. As judged from the chemical properties of these two substituents, they can be functionalized, thereby modifying the properties of the parent nanomolecules [5]. The dendrimers of our interest are mainly characterized by multinuclear NMR (especially ^{31}P NMR), whereas such mass spectral techniques as MALDI–TOF proved unfeasible here, since laser irradiation partially destroyed the denrimer molecules [6]. Fourier-transform IR and Raman spectroscopy proved to be the most interesting and appropriate analytical techniques, and they formed the basis for the long-term and fruitful collaboration between the research groups from Toulouse and Kazan [7]. In particular, we have performed an experimental and theoretical (DFT) research [8] on the effect of the generation [9] and core of dendrimers {P(S), vinyl [10], N_3P_3 [11]} on their structure.

Quite recently we initiated studies of surface functional groups of dendrimers [12]. To this end, we synthesized two novel families of organophosphorus dendrimers containing surface phenoxy and pentadeuterophenoxy groups. The phenoxy group was chosen, since it was expected to be readily added to the $P(S)Cl_2$ groups of our dendrimers and also due to the commercial availability of its fully deuterated analog; thus we could compare structurally similar substituents with different spectral signatures. Moreover, the phenoxy group can be considered as "neutral" with respect to the structure of dendrimers, i.e. it should slightly affect their properties. The present paper described the synthesis of the two novel families, each containing sixth generation dendrimers.

EXPERIEMNTAL

The synthesis and all subsequent operations were performed in vacuum devices under dry argon. All solvents were preliminarily dried and distilled (THF and ether on Na/benzophenone, and pentane and dichloromethane on P_2O_5).

The ^1H, ^{13}C, and ^{31}P NMR spectra were measured in $CDCl_3$ on Bruker ARX250, AV300, AV400, and AV500 spectrometers against 85% H_3PO_4 (^{31}P) and $SiMe_4$ (^1H and ^{13}C). The ^1H and ^{13}C NMR spectra were registered using the J_{mod} and two-dimensional HMBC and HMQC techniques (when necessary); the ^{31}P NMR spectra were registered using broad-band proton decoupling or CW decoupling. Dendrimers 1-G_n dendrimers were synthesized as described in [13]. In the assignment of NMR spectra we made use of the atom numbering shown in Fig. 1.

Synthesis of Compounds 2-G_0 and 2-G_{0D}

Phenol and phenol-d_5, 1.0 g, and 4 g of cesium carbonate were added to a solution of 0.5 g of hexachlorotriphosphazene in 50 ml of THF. The resulting mixture was stirred overnight at ambient temperature and then further centrifuged for 30 min at 10000 rpm. The supernatant was collected, filtered through Celite, and dried at reduced pressure. Excess phenol was evaporated at reduced pressure, and the oily residue was purified by liquid chromatography on silica gel (eluent hexane–ethyl acetate, 3:1). Pure fractions were collected and dried; as a result, transparent crystals were obtained.

Compound 2-G_0 [16]. Yield 70%. ^1H NMR spectrum, δ, ppm: 7.26–7.13 m (18H, C_c-H, C_d-H), 7.00 d ($^3J_{HH}$ 8.3 Hz, 12H, C_b). $^{31}P\{^1H\}$ NMR spectrum, δ_P, ppm: 11.5 (P_0). $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 150.7 d ($^2J_{CP}$ 8.3 Hz, C_a), 129.5 (C_c), 124.9 (C_d), 121.1 (C_b).

Compound 2-G_{0D}. Yield 73%. ^1H NMR spectrum, δ, ppm: 7.28–7.03 (undeuterated phenol residue). ^{31}P

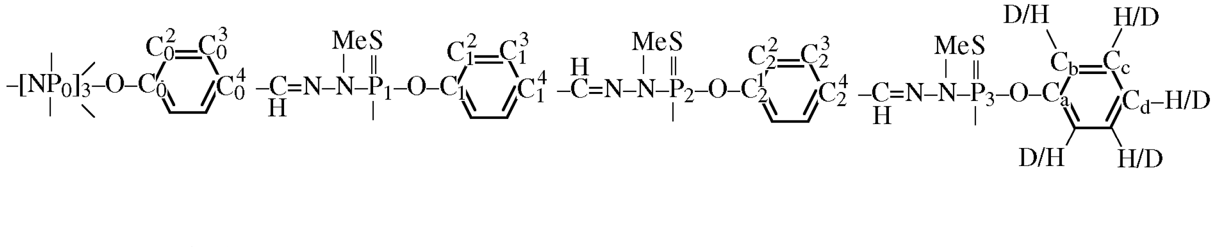


Fig. 1. Atom numbering used in the assignment of NMR signals of generation 3 dendrimers.

$\{^1H\}$ NMR spectrum, δ_P, ppm: 11.5. $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 150.6 (C_a), 128.9 (t_D, $^1J_{CD}$ 24.4 Hz, C_c), 124.3 (t_D, $^1J_{CD}$ 23.9 Hz, C_d), 120.7 (t_D, $^1J_{CD}$ 24.4 Hz, C_b).

Synthesis of Dendrimers 2-G_n and 2-G_{nD} with Phenol End Froups

A dendrimer with $P(S)Cl_2$ end groups, 0.5 g, was dissolved in 30 ml of distilled THF containing 1.2 equiv (by chlorine) of phenol and 2.4 equiv of cesium carbonate. The mixture was stirred overnight at ambient temperature. After centrifuging, the supernatant was filtered on Celite, reduced to 3 ml, and diluted with 150 ml of pentane. A white precipitate formed and was filtered off and washed with pentane (3×150 ml).

Compound **2-G_1**. Yield 81%. ^1H NMR spectrum, δ, ppm: 7.59 d ($^3J_{HH}$ 8.6 Hz, 12H, C_0^3H), 7.53 d ($^3J_{HP}$ 1.4 Hz, 6H, CH=N), 7.21 m (60H, C_6H_5), 6.97 d ($^3J_{HH}$ 8.6 Hz, 12H, C_0^2H), 3.21 d ($^3J_{HP}$ 10.3 Hz, 18H, CH_3NP). $^{31}P\{^1H\}$ NMR spectrum, δ_P, ppm: 66.0 (P_1), 11.9 (P_0) . $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 151.1 (C_0^1), 150.6 (C_a), 138.4 d ($^3J_{CP}$ 14.0 Hz, CH=N), 132.2 (C_0^4), 129.5 (C_c), 128.2 (C_0^3), 125.4 (C_d), 121.4 ($C_0{}^2$), 121.3 (C_b), 33.0 d ($^2J_{CP}$ 12.3 Hz, CH_3NP).

Compound **2-G_{1D}**. Yield 85%. ^1H NMR spectrum, δ, ppm: 7.60 m (18H, $C_0{}^3H$, CH=N), a signal of incompletely deuterated phenol, 6.90 d ($^3J_{HH}$ 8.4 Hz, 12H, $C_0{}^2H$), 3.20 s ($^3J_{HP}$ 10.3 Hz, 18H, CH_3NP). $^{31}P\{^1H\}$ NMR spectrum, δ_P, ppm: 66.1 (P_1), 11.8 (P_0). $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 151.6 m (C_a), 150.9 d ($^2J_{CP}$ 5.0 Hz, C_0^1), 138.8 d ($^3J_{CP}$ 14.1 Hz, CH=N), 132.6 (C_0^4), 129.5 (t_D, $^1J_{CD}$ 24.7 Hz, C_c), 128.7 (C_0^3), 125.3 (t_D, $^1J_{CD}$ 22.1 Hz, C_d), 121.8 (C_0^2), 121.4 (t_D, $^1J_{CD}$ 24.2 Hz, C_b), 33.4 d ($^2J_{CP}$ 12.4 Hz, CH_3NP).

Compound **2-G_2**. Yield 78%. ^1H NMR spectrum, δ, ppm: 7.56 m (54H, CH_{Ar}, CH=N), 7.19 m (120H, C_6H_5), 6.78 m (36H, CH_{Ar}), 3.24 d ($^3J_{HP}$ 10.3 Hz, 36H, CH_3NP_2), 3.16 d ($^3J_{HP}$ 6.8 Hz, 18H, CH_3NP_1). $^{31}P\{^1H\}$ NMR spectrum, δ_P, ppm: 66.1 (P_2), 65.9 (P_1), 12.0 (P_0). $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 151.1 d ($^2J_{CP}$ 6.4 Hz, C_a, C_0^1), 150.5 d ($^2J_{CP}$ 7.1 Hz, C_1^1), 138.4 d ($^3J_{CP}$ 14.0 Hz, CH=N), 132.3 (C_1^4, C_0^4), 129.5 (C_c), 128.2 (C_1^3, C_0^3), 125.4 (C_d), 121.6 (C_1^2, C_0^2), 121.3 (C_b), 33.0 d ($^2J_{CP}$ 12.7 Hz, CH_3NP).

Compound **2-G_{2D}**. Yield 88%. ^1H NMR spectrum, δ, ppm: 7.60 m (54H, CH_{Ar}, CH=N), 7.22 m (36H, CH_{Ar}), 3.25 d ($^3J_{HP}$ 10.2 Hz, 36H, CH_3–N–P_2), 3.20 d ($^3J_{HP}$ 10.1 Hz, 18H, CH_3–N–P_1). $^{31}P\{^1H\}$ NMR spectrum, δ_P, ppm: 66.1 (P_2), 65.9 (P_1), 11.9 (P_0). $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 151.6 (C_a), 150.8 (C_1^1, C_0^1), 139.3 d ($^3J_{CP}$ 15.1 Hz, CH=NNP$_1$), 138.8 d ($^3J_{CP}$ 14.1 Hz, CH=NNP$_2$), 132.8 (C_1^4), 132.5 (C_0^4), 129.5 (t_D, $^1J_{CD}$ 23.6 Hz, C_c), 128.7 ($C_1{}^3$, C_0^3), 125.3 (t_D, $^1J_{CD}$ 23.3 Hz, C_d), 122.2 (C_1^2), 121.9 (C_0^2), 121.4 (t_D, $^1J_{CD}$ 24.7 Hz, C_b), 33.5 d ($^2J_{CP}$ 12.4 Hz, CH_3NP).

Compound **2-G_3**. Yield 78%. ^1H NMR spectrum, δ, ppm: 7.85–6.80 m (450H, C_6H_5, CH_{Ar}, CH=N), 3.20 m (126H, CH_3NP). $^{31}P\{^1H\}$ NMR spectrum, δ_P, ppm: 66.0 (P_3), 65.8 (P_1, P_2), 11.8 (P_0). $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 151.2 (C_a, C_1^1, C_0^1), 150.7 d ($^2J_{CP}$ 5.1 Hz, C_2^1), 138.6 d ($^3J_{CP}$ 13.4 Hz, CH=N), 132.3 (C_2^4, C_1^4, C_0^4), 129.5 (C_c), 128.2 (C_2^3, C_1^3, C_0^3), 125.4 (C_d), 121.7 (C_2^2, C_1^2, C_0^2), 121.4 (C_b), 33.2 d ($^2J_{CP}$ 12.8 Hz, CH_3NP).

Compound **2-G_{3D}**. Yield 56%. ^1H NMR spectrum, δ, ppm: 7.92–6.82 m (210H, CH_{Ar}, CH=N), 3.30–3.00 m (126H, CH_3NP). $^{31}P\{^1H\}$ NMR spectrum, δ_P, ppm: 66.1 (P_1), 66.0 (P_3), 65.9 (P_2), 11.8 (P_0). $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 151.5 d ($^2J_{CP}$ 6.0 Hz, C_a), 150.9 d ($^2J_{CP}$ 7.0 Hz, C_2^1, C_1^1, C_0^1), 139.5 m (CH=N), 138.9 d ($^3J_{CP}$ 13.0 Hz, CH=NNP$_3$), 132.7 (C_2^4, C_1^4, C_0^4), 129.5 (t_D, $^1J_{CD}$ 25.1 Hz, C_c), 128.7 (C_2^3, C_1^3, C_0^3), 125.3 (t_D, $^1J_{CD}$ 23.9 Hz, C_d), 122.2 (C_2^2, C_1^2, C_0^2), 121.4 (t_D, $^1J_{CD}$ 24.1 Hz, C_b) 33.4 d ($^2J_{CP}$ 13.1 Hz, CH_3NP).

Compound **2-G_4**. Yield 76%. ^1H NMR spectrum, δ, ppm: 7.92–6.81 m (930H, C_6H_5, CH_{Ar}, CH=N), 3.19 m (270H, CH_3NP). $^{31}P\{^1H\}$ NMR spectrum, δ_P, ppm: 66.1 (P_1, P_2, P_3, P_4), 11.8 (P_0). $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 151.2 d ($^2J_{CP}$ 7.1 Hz, C_a, C_{0-2}^1), 150.5 d ($^2J_{CP}$ 7.0 Hz, $C_3{}^1$), 138.7 m (CH=N), 132.3 (C_{0-3}^4), 129.5 (C_c), 128.2 ($C_{0-3}{}^3$), 125.4 (C_d), 121.8 (C_{0-3}^2), 121.4 d ($^3J_{CP}$ 4.1 Hz, C_b), 33.1 d ($^2J_{CP}$ 12.7 Hz, CH_3NP).

Compound **2-G_{4D}**. Yield 75%. ^1H NMR spectrum, δ, ppm: 7.85–7.00 m (450H, CH_{Ar}, CH=N), 3.40–3.00 m (270H, CH_3NP). $^{31}P\{^1H\}$ NMR spectrum, δ_P, ppm: 65.8 (P_1, P_2, P_3, P_4), 11.8 (P_0). $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 151.6 d ($^2J_{CP}$ 6.0 Hz, C_a), 150.8 d ($^2J_{CP}$ 7.0 Hz, $C_{0-3}{}^1$), 139.5 d ($^3J_{CP}$ 12.1 Hz, CH=NNP), 139.9 d ($^3J_{CP}$ 14.1 Hz, CH=NNP$_4$), 132.7 (C_{0-3}^4), 129.5 (t_D, $^1J_{CD}$ 23.6 Hz, C_c), 128.7 (C_{0-3}^3), 125.4 (t_D, $^1J_{CD}$ 24.1 Hz, C_d), 122.2 (C_{0-3}^2), 121.4 (t_D, $^1J_{CD}$ 22.5 Hz, C_b), 33.4 d ($^2J_{CP}$ 12.5 Hz, CH_3NP).

Compound 2-G_5. Yield 79%. ^1H NMR spectrum, δ, ppm: 7.90–7.10 m (1890H, C_6H_5, CH_{Ar}, CH=N), 3.19 s (558H, CH_3NP). $^{31}P\{^1H\}$ NMR spectrum, δ_P, ppm:

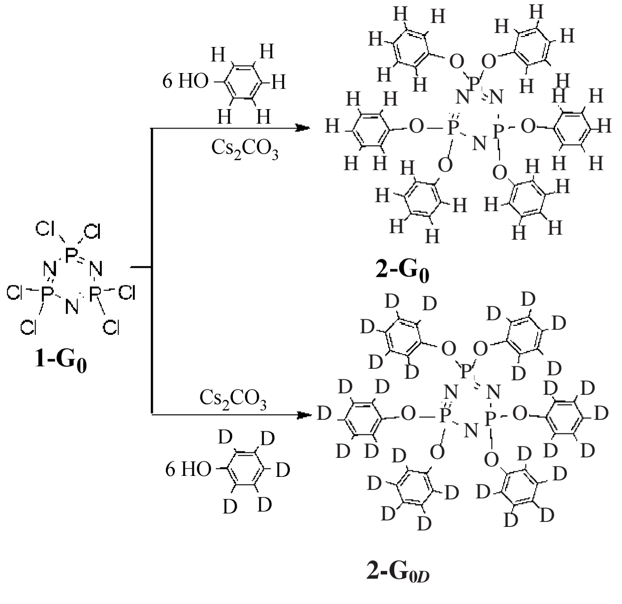
65.9 (P_5), 65.7 (P_1, P_2, P_3, P_4). $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 150.8 m (C_a, C^1_{0-4}), 138.8 (CH=N), 132.2 (C^4_{0-4}), 129.5 (C_c), 128.2 (C^3_{0-4}), 125.4 (C_d), 122.1 (C^2_{0-4}), 121.3 (C_b), 33.0 m (CH_3NP).

Compound ***2-G$_{5D}$***. Yield 84%. ^1H NMR spectrum, δ, ppm: 7.95–6.8 m (930H, CH_{Ar}, CH=N), 3.35–3.00 m (558H, CH_3NP). $^{31}P\{^1H\}$ NMR spectrum, δ_P, ppm: 65.9 (P_5), 65.7 (P_4, P_3, P_2, P_1). $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 151.7 m (C_a), 150.8 m (C^1_{0-4}), 139.6 m (CH=N), 138.9 d ($^3J_{CP}$ 12.0 Hz, $CH=NNP_5$), 132.7 (C^4_{0-4}), 129.5 (t_D, $^1J_{CD}$ 24.1 Hz, C_c), 128.7 (C^3_{0-4}), 125.3 m (C_d), 122.2 (C^2_{0-4}), 121.5 (t_D, $^1J_{CD}$ 22.2 Hz, C_b), 33.5 d ($^2J_{CP}$ 13.1 Hz, CH_3NP).

Compound ***2-G$_6$***. Yield 87%. ^1H NMR spectrum, δ, ppm: 7.90–6.85 (sl, 3810H, C_6H_5, CH_{Ar}, CH=N), 3.19 (sl, 1134H, CH_3NP). $^{31}P\{^1H\}$ NMR spectrum, δ_P, ppm: 65.7 (P_1, P_2, P_3, P_4, P_5). $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 150.8 m (C_a, C^1_{0-5}), 138.8 m (CH=N), 132.2 (C^4_{0-5}), 129.5 (C_c), 128.2 (C^3_{0-5}), 125.4 (C_d), 122.1 (C^2_{0-5}), 121.3 (C_b), 33.2 m (CH_3NP).

Compound ***2-G$_{6D}$***. Yield 85%. ^1H NMR spectrum, δ, ppm: 7.90–6.85 (sl, 1890H, CH_{Ar}, CH=N), 3.19 sl (1134H, CH_3NP). $^{31}P\{^1H\}$ NMR spectrum, δ_P, ppm: 65.8 (P_1, P_2, P_3, P_4, P_5). $^{13}C\{^1H\}$ NMR spectrum, δ_C, ppm: 151.6 m (C_a), 150.9 m (C^1_{0-5}), 139.6 m (CH=N), 139.0 ($CH=NNP_6$), 132.7 (C^4_{0-5}), 129.5 (t_D, $^1J_{CD}$ 24.1 Hz, C_c), 128.7 (C^3_{0-5}), 125.4 m (C_d), 122.2 (C^2_{0-5}), 121.4 (t_D, $^1J_{CD}$ 22.6 Hz, C_b), 33.5 m (CH_3NP).

Scheme 1. Synthesis of generation 0 dendrimers



1-G$_0$

2-G$_0$

2-G$_{0D}$

RESULTS AND DISCUSSION

NMR Control During Synthesis of Dendrimers

The synthesis was started with $N_3P_3Cl_6$ which was used as a core, by repeating two simple and quantitative reactions: nucleophilic substitution via 4-hydroxybenzaldehyde in a basic medium and condensation between aldehydes and the phosphorus-containing hydrazide $H_2NNMeP(S)Cl_2$. Dendrimers with either aldehyde or $P(S)Cl_2$ end groups were previously synthesized to the eighth generation [13].

The substitution reaction was initially performed directly on the $N_3P_3Cl_6$ core (1-G$_0$) of the zero-generation dendrimer, using 6 equiv of phenol or phenol-d_5 in the presence of cesium carbonate as an inotganic base (Scheme 1).

Reaction progress was followed by ^{31}P NMR; initially, the spectrum contained many signals from different AA'B systems, associated with consecutive substitution of Cl by phenolic residues. Upon completion of all substitution reactions, the ^{31}P NMR spectra contained a single singlet ay 11.5 ppm in both cases (2-G$_0$ and 2-G$_{0D}$).

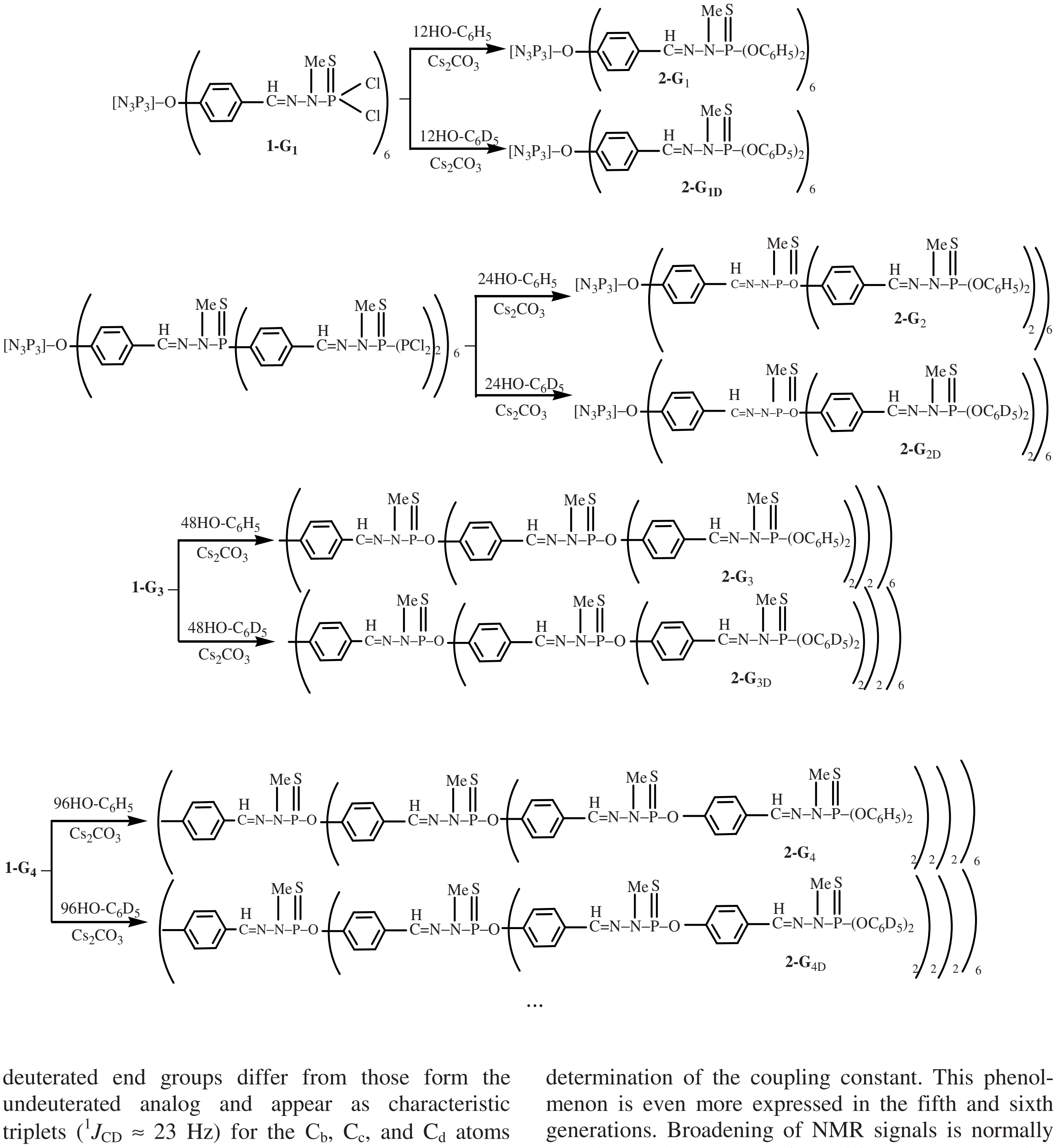
The same substitution reactions were performed in generation 1–6 phosphorus-containing dendrimers 1-G$_n$ (*n* 1–6) in the presence of cesium carbonate, using phenol or phenol-d_5 (Scheme 2).

In all cases, the signal of end $P(S)Cl_2$ groups (δ_P 64 ppm) gradually converted into a signal at δ_P 71 ppm, corresponding to the P(S)ClOAr group. Finally, a signal at δ_P 66 ppm appeared, which evidenced the reaction completion and the formation of $P(S)(OAr)_2$. ^{31}P NMR spectroscopy allows direct monitoring substitution progress at all terminal groups of the dendrimer with an accuracy of up to 0.5%. Moreover, signals related to different generations are readily distinguishable up to the third generation (Fig. 2).

Structural Characterization of Dendrimers

All the dendrimers obtained were characterized by means of ^1H and ^{13}C NMR. The proton NMR technique is poorly informative, since the aromatic and hydrazone groups, on the one hand, and methyl group, on the other, are impossible to distinguish. By contrast, ^{13}C NMR shows interesting results. First of all, both the dendrimer families give signals in the same regions. However, the signals of dendrimers with

Scheme 2. Synthesis of generations 1 to 6 dendrimers



deuterated end groups differ from those form the undeuterated analog and appear as characteristic triplets ($^1J_{CD}$ ≈ 23 Hz) for the C_b, C_c, and C_d atoms (Fig. 1). These features allow identification of signals of end group. Detailed examination of these three signals shows that one of them is especially sensitive to generation. Actually, the signal of the C_d carbon (which is *para* with respect to oxygen) gets broader in the fourth generation, which makes difficult determination of the coupling constant. This phenolmenon is even more expressed in the fifth and sixth generations. Broadening of NMR signals is normally associated with a loss of mobility. Our observation provides clear evidence for enhancing steric hindrances in dendrimers, beginning with the fourth generation. Two hypotheses can be suggested to explain this phenomenon: (1) some real steric hindrance on the surface or (2) certain functional

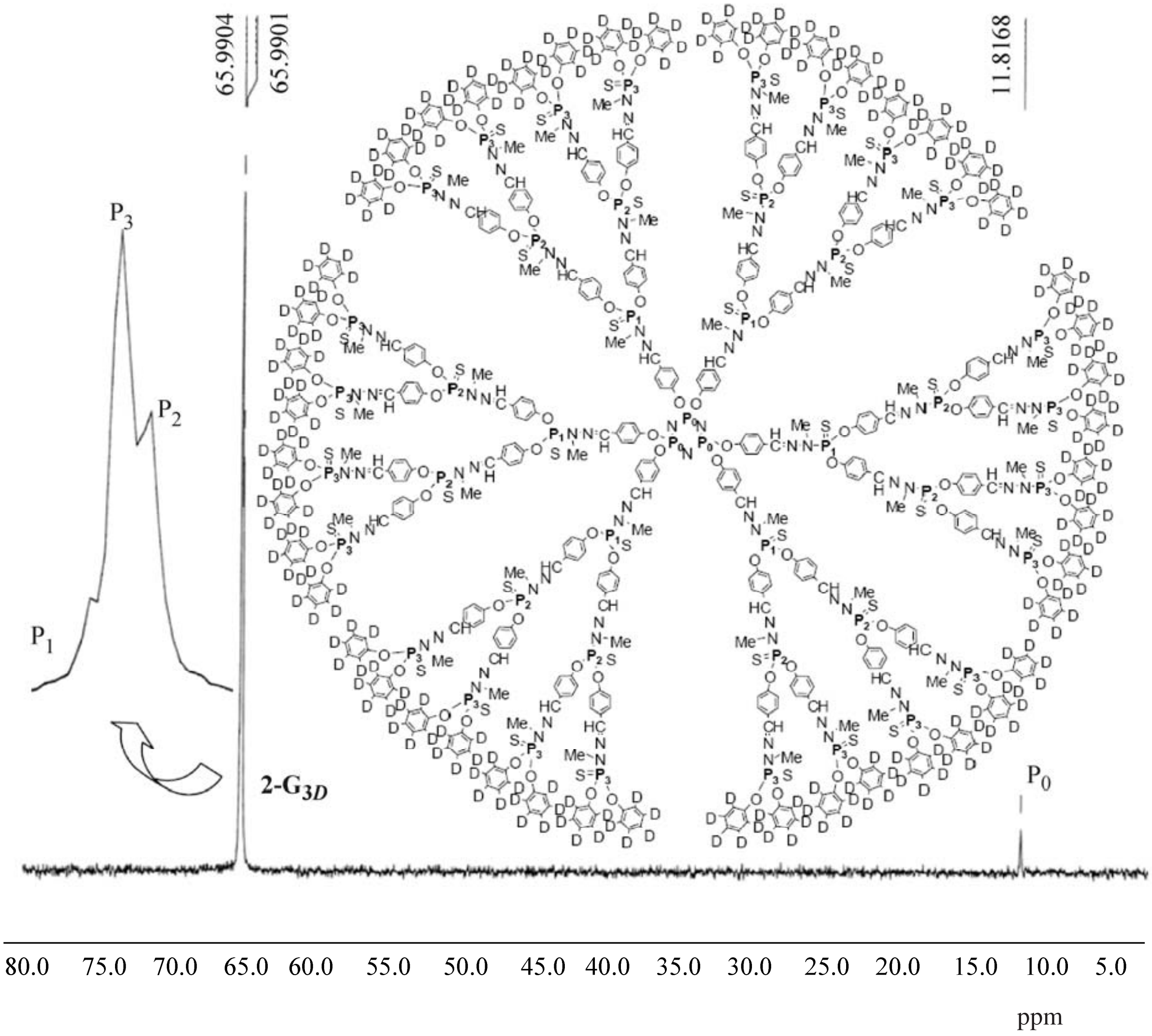


Fig. 2. ^{31}P NMR spectrum of generation 3 dendrimer **2-G$_{3D}$**.

groups turn inward the structure, which is facilitated with increasing generation, on account of increasing flexibility of branches with their elongation.

To obtain evidence for the suggested steric hindrance, we made use of IR spectroscopy. This method provides solid-state data, whereas ^{13}C NMR gives information about the state in solution. The IR spectra of the zero-generation **2-G$_0$** and **2-G$_{0D}$** were assigned using DFT calculations [11]. The resulting data were also used to assign the IR spectra of further generation dendrimers. Such approach gave us evidence to show that the IR bands of surface functional groups are the most informative.

Actually, the number of functional groups increases by two for each further generation, and the corresponding bands should follow this simple arithmetic progression, unless other factors are considered (such as medium, conformation, and intra- and intermolecular interactions). Of these factors, the flexibility of the fragments in question will be affected by those that affect the lifetime of vibration levels, and, as a result, the shape and width of the corresponding IR bands. Such analysis, especially detailed for dendrimers **2-G$_{nD}$**, revealed only slight changes in the IR spectra of the internal part of dendrimers of any generation (probably, the zero generation is an exception). This finding means that the shape and conformation of internal branches scarcely change with changing molecular size or generation number. By contrast, the width of the IR bands of surface groups varies with generation. In higher generations, beginning with the fourth, the conformation of end groups is violated due to steric hindrances [12].

CONCLUSIONS

Two novel families of opganophosphorus dendrimers of generations 0 to 6, with similar surface functional groups (phenoxy and deuterophenoxy) were synthesized, aimed at gaining further insight into the structure of such nanomolecules. Solution ^{13}C NMR and solid-state IR studies led us to two converging conclusions: steric hindrances associated with surface functional groups begin to reveal themselves in the fourth generation (96 end functional groups), are well defined in the fifth and sixth generation (192 and 384 end functional groups, respectively). This phenomenon has been studied for years to obtain contradictory results for dendrimers of different types [14]. It should be noted that steric hindrances in these generatyions of phosphorus-containing dendrimers are still not strong enough to prevent further synthesis involving surface functional groups (^{31}P NMR data), block the surface, and prevent penetration of solvent molecules into the structure. We previously showed that this phenomenon is associated with quasitotal disappearance of spectral signals from the internal structure [15], but this is not observed in our present case.

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