J Math Chem (2010) 48:566–582
DOI 10.1007/s10910-010-9692-4

ORIGINAL PAPER

Molecular geometry and conformation: mathematical relations between intra-molecular distances and conformation in Fréchet-type dendrimers and dendrons

Adrian-Mihail Stadler

Received: 21 December 2009 / Accepted: 26 April 2010 / Published online: 27 June 2010

Abstract A geometrical approach to two distances in Fréchet-type dendrimers is presented in this paper: the dependence on the conformation of the distance between the centres of two consecutive phenyls (i.e. the two phenyl rings of a benzyl-phenyl-ether motif), and the calculation of the radius of a G1 dendron (i.e. the distance between the C1 atom of the focal phenyl ring and the C4 atom of a phenyl ring superior to it), as a function of torsion angles. This approach enables determination of the extreme values of these distances.

Keywords Dendrimers · Fréchet-type dendrimers · Molecular geometry · Conformation · Torsion angle

1 Introduction

The increasing evolution of the research concerning dendrimers [1–7]—that are molecules with a branched tree-like structure—in particular with respect to their applications related to medicine [8] (oncology [9], gene delivery [10–13], drug research [14–17]), to catalysis [18–22], to metallo-dendrimers [23–28], to organic light-emitting diodes [29,30] etc., explains the actual interest for the structural aspects of dendritic

Dedicated to Eng. Aurelian Niculescu on the occasion of his birthday.

A.-M. Stadler (✉)
Institut de Science et d'Ingénierie Supramoléculaires, Université de Strasbourg,
8 Allée Gaspard Monge, 67083 Strasbourg, France
e-mail: mstadler@isis.u-strasbg.fr

A.-M. Stadler
Karlsruhe Institute of Technology (KIT), Forschungszentrum Karlsruhe (FZK),
Institute for Nanotechnology (INT), Postfach 3640, 76021 Karlsruhe, Germany

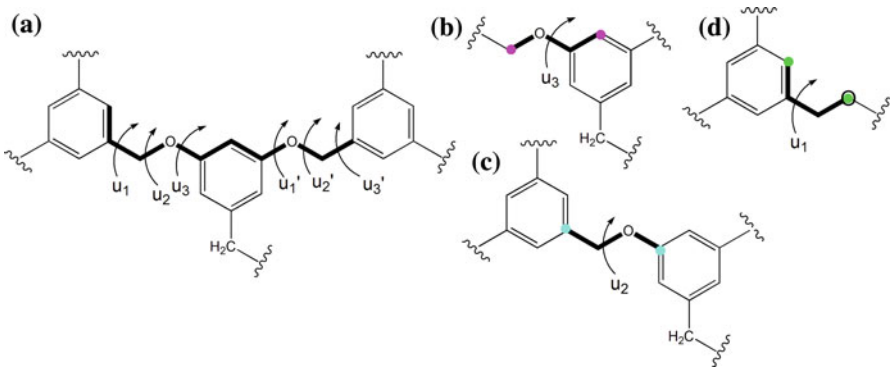

Fig. 1 **a** The six torsion angles u_1, u_2, u_3, u'_1, u'_2 and u'_3 that are responsible of the conformation of a 1-substituted-3,5-di(benzyloxy)benzene unit; **b** u_3; **c** u_2; **d** u_1

molecules. This results from numerous studies through theoretical calculations [31–39], NMR [40,41], solvatochromic methods [42], fluorescence [43], size exclusion chromatography [44] etc.

Fréchet-type dendrimers are a class of dendrimers based on 1-substituted-3,5-di(benzyloxy)benzene. Their convergent synthesis [45–48] induced intense development of this field, among the numerous subjects of research being, for example: synthetic hosts obtained by monomolecular imprinting inside dendrimers [49], new classes of polyether dendritic fragments [50–52], photosensitizers for photodynamic therapy based on light-harvesting ionic Fréchet-dendrimer porphyrins [53], structurally diverse dendritic libraries [54] etc.

The study of the conformation (for a case of conformational duality in the solid state, see ref. [55]) of Fréchet-type dendrimers is of importance for aspects like their three-dimensional structure, their planarity, their spatial demand [56], their self-assembly [57–60], their catalytic properties [61], crystal engineering [62], surface studies [63–65], solid-state nuclear magnetic resonance studies [66,67].

The global conformation of Fréchet-type dendrimers is a collection of conformations of the 1-substituted-3,5-di(benzyloxy)benzene units that compose the dendrimer. The conformation of these units depends on a set of six torsion angles: u_1, u_2, u_3, u'_1, u'_2 and u'_3 (Fig. 1).

Intra-molecular distances [68] often depend on the conformation and consequently on the torsion angles. It is possible to deduce the mathematical relation between distances and torsion angles. Such relations may find applications, for example, in molecular modelling. Moreover, it is of interest to deduce the molecular conformation (torsion angles) starting from molecular dimensions experimentally measured and using mathematical relations that link molecular dimensions to torsion angles.

The aim of this paper is to report the demonstration of two mathematical expressions:

(1) the dependence on the conformation of the distance between the centres of two consecutive phenyls (i.e. the two phenyl rings of a benzyl-phenyl-ether motif), and

(2) the calculation of the radius of a G1 dendron (i.e. the distance between C1 atom of the focal phenyl ring and the C4 atom of a phenyl ring superior to it), as a function of torsion angles.

This approach enables determination of the extreme values of these distances. In all calculations herein reported the angles are in degrees.

2 The dependence on the conformation of the distance between the centres of the phenyl rings of a benzyl-phenyl-ether motif

2.1 Motivation

The mathematical relation between the distance z between the centres of the phenyl rings of a benzyl-phenyl-ether, and the torsion angle on which depends this distance, may be useful where a dendrimer or dendron is represented as a model [69] consisting of beads corresponding to phenyl rings connected by distances that depend on the torsion angle u_2 or u'_2 (Fig. 2).

The centres of the concerned phenyl rings are located on the axis of torsion angles u_1 or u'_1, respectively u_3 or u'_3. Consequently the distance between these centres does not depend on the mentioned angles, but only on u_2 or u'_2.

2.2 Calculation

The calculation of the distance z as a function of the torsion angle u_2 (or u'_2) is based on a sequence of three lengths (a, b, c), the torsion angle u_2, the plane P_1 that contains a and b, the plane P_2 that contains b and c, and the line $P_1 \cap P_2$ at the intersection of P_1 with P_2. The angles (in degrees) between a and b, and respectively b and c, are u_{ab}, respectively u_{bc}. The angle between the planes P_1 and P_2 is the torsion angle u_2 (or u'_2) (Fig. 3a).

Let e be perpendicular to $P_1 \cap P_2$ (Fig. 3b). Then

$$e = a*\sin(180 - u_{ab}) = a*\sin(u_{ab}) \tag{1}$$

e belongs to the right triangle of sides a, e and d, where

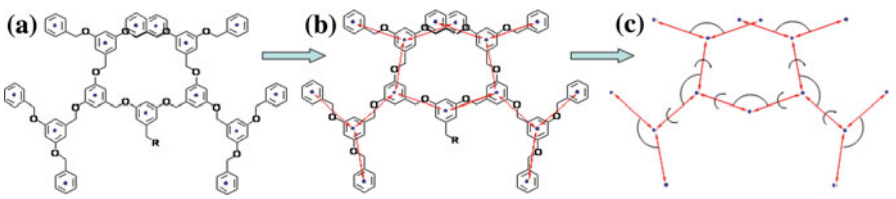

Fig. 2 **a** A G3 Fréchet-type dendron and the centres of its phenyl rings; **b** representation of the distances between the centres; **c** representation of the centres of phenyl rings, of the distances between them and of the angles defined by these distances

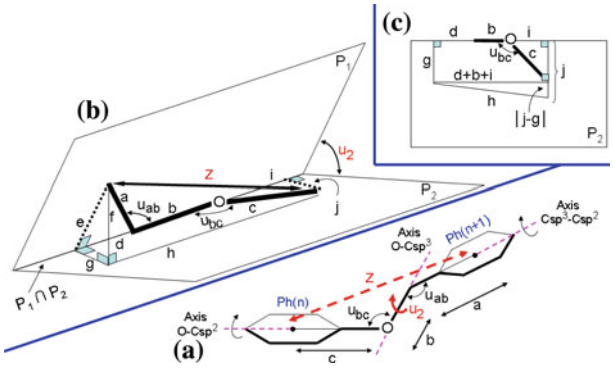

Fig. 3 **a** Distance between the centres of the phenyl rings of a benzyl-phenyl-ether motif; **b** geometrical parameters of a torsion angle u_2: a, b, c are the sides of the angle, u_{ab}, u_{bc} are the corresponding angles; **c** geometrical details of the plane P_2

$$d = a*\cos(180 - u_{ab}) = -a*\cos(u_{ab}) \tag{2}$$

Let j be perpendicular to $P_1 \cap P_2$ (Fig. 3b), so

$$\begin{aligned} j &= c*\sin(180 - u_{bc}) = c*\sin(u_{bc}) \text{ and } i = c*\cos(180 - u_{bc}) \\ &= -c*\cos(u_{bc}) \end{aligned} \tag{3}$$

Let f be perpendicular to P_2. As $e \perp (P_1 \cap P_2)$ and $g \perp (P_1 \cap P_2)$, then

$$f = e*\sin(u_2) = a*\sin(u_{ab})*\sin(u_2) \text{ and } g = a*\sin(u_{ab})*\cos(u_2) \tag{4}$$

Depending on the values of a, b, c, u_{ab}, u_{bc} and u_2, there may be $j < g$ or $g < j$, but the value $(j - g)^2$ employed further, is positive.

In the right triangle of which sides are h, d+b+i and j−g (Fig. 3c), the Pythagorean theorem, and (1), (2) and (3) give:

$$\begin{aligned} h^2 = (d + b + i)^2 + (j - g)^2 &= [-a*\cos(u_{ab}) + b - c*\cos(u_{bc})]^2 \\ &+ [-c*\cos(u_{bc}) - a*\sin(u_{ab})*\cos(u_2)]^2 \end{aligned} \tag{5}$$

$f \perp P_2$ and $h \subset P_2$, then $f \perp h$. So $z = (f^2 + h^2)^{1/2}$. This last equality together with (4) and (5) gives: $z = [f^2 + (d + b + i)^2 + (j - g)^2]^{1/2} = \{a^2 * \sin^2(u_{ab})*\sin^2(u_2) + [-a*\cos(u_{ab}) + b - c*\cos(u_{bc})]^2 + [c*\cos(u_{bc}) - a*\sin(u_{ab})*\cos(u_2)]^2\}^{1/2} = \{[-a*\cos(u_{ab}) + b - c*\cos(u_{bc})]^2 + a^2 * \sin^2(u_{ab}) + c^2 * \sin^2(u_{bc}) - 2ac*\sin(u_{ab})*\sin(u_{bc})*\cos(u_2)\}^{1/2}$

Thus:

$$z = [m_1 - m_2*\cos(u_2)]^{1/2} \tag{6}$$

where $m_1 = [-a*\cos(u_{ab}) + b - c*\sin(u_{bc})]^2 + a^2 * \sin^2(u_{ab}) + c^2 * \sin^2(u_{bc})$, and $m_2 = 2ac*\sin(u_{ab})\sin(u_{bc})$.

Table 1 Examples of application of the formula for calculation of the distance z

Structure code	u_2(°)	z_{calc} (Å)	z_{meas} (Å)	$\lvert z_{calc} - z_{meas} \rvert$ (Å)	$100*\lvert z_{calc} - z_{meas} \rvert / z_{meas}$ (%)
BEQQUK	−179.5	6.327	6.374	0.047	0.737
	177.82	6.326	6.362	0.036	0.566
	−71.39	4.733	4.977	0.244	4.903
	175.14	6.323	6.355	0.032	0.504
	158.23	6.251	6.258	0.007	0.112
	171.34	6.315	6.358	0.043	0.676
CAZVAB	−177.31	6.326	6.371	0.045	0.706
EDEWUG	−174.21	6.321	6.373	0.052	0.816
	169.77	6.310	6.334	0.024	0.379
FAVGIT	169.39	6.309	6.305	0.004	0.056
	177.58	6.326	6.369	0.043	0.675
IXEKIF	−179.57	6.327	6.367	0.04	0.628
	178.45	6.326	6.276	0.05	0.797
LIHPAU	73.05	4.771	5.031	0.26	5.168
	77.36	4.872	5.1	0.228	4.471
WIBXEL	−70.15	4.704	4.919	0.215	4.371
	78.52	4.899	5.168	0.269	5.205

If z is known, then the corresponding torsion angle u_2 is: $u_2 = \arccos[(m_1 - z^2)/m_2]$.

The average values to be considered are a = 2.89Å, b = 1.43Å [70], c = 2.75Å, $u_{ab} = 109.5°$ and $u_{bc} = 117°$. The formula for the centroid-to-centroid distance z is:

$$z = [26.67 - 13.36*\cos(u_2)]^{1/2} \tag{7}$$

2.3 Verification

The formula for calculation of z was applied to a set of values of u_2 obtained from published X-ray structures of which CSD codes are (Table 1): BEQQUK [71], CAZVAB [72], EDEWUG [73], FAVGIT [74], IXEKIF [75], LIHPAU [76], WIBXEL [77]. The angles and distances were measured through the software Mercury. The average of the differences between calculated and measured values $\lvert z_{calc} - z_{meas} \rvert$ is 0.096 Å. For each measure, a percentage was calculated with the formula $100* \lvert z_{calc} - z_{meas} \rvert / z_{meas}$; the average of these percentages is 1.810%.

2.4 Extrema

The calculation of the extrema passes through the equation $z' = 0$, i.e. $z' = 0.5m_2*\sin(u_2)/[m_1 - m_2 * \cos(u_2)]^{1/2} = 0$, that gives $\sin(u_2) = 0$, so $u_2 = 0°$, respectively $u_2 = \pm 180°$ to which correspond the extrema 3.64 Å, respectively 6.32 Å.

3 The radius of a G1 dendron as a function of torsion angles

3.1 Motivation

This calculation was inspired by the method utilized in a paper due to the group of Professor A.-D. Schlüter to estimate the dimensions and the space demand of the G2 dendron of which CSD code is RISZIC [78]. For this purpose, the radius and the diameter of the cylinder partially filled by the dendron were evaluated by measuring the distances between the carbon C1 of the phenyl ring of G0 level and the carbon C4 of the phenyl rings of G2 level (Fig. 4a). This distance depends on several torsion angles and its calculation appears mathematically quite laborious.

The calculation reported here concerns a simpler case that deals with the radius y (Fig. 4b, c) of a smaller dendron (a G1 one), i.e. the distance between the carbon C1 of a phenyl ring of G0 level and the carbon C4 of one of the two G1 phenyl rings (Fig. 4b, c). As defined here, the radius y is not the radius from the Stokes-Einstein equation.

The aim is to deduce how this radius depends on the conformation through the torsion angles.

Starting from this radius one may estimate the volume of the dendron as a function of torsion angles (*vide infra* 3.5).

Correlatively, the determination of this volume through a physical method may further lead to the radius y. From this, thanks to the mathematical relation between y and the torsion angles on which depends y, one may get information about the conformation.

The demonstration presented here is also an example of geometrical analysis of a conformational motion that depends on two torsion angles.

3.2 Calculation

Among the three types of torsion angles u_1, u_2 and u_3, this radius (Figs. 4b and 5), noted y or B′I, depends only on u_2 and u_3. It does not depend on u_1, because one of its ends is located on the rotational axis of this angle.

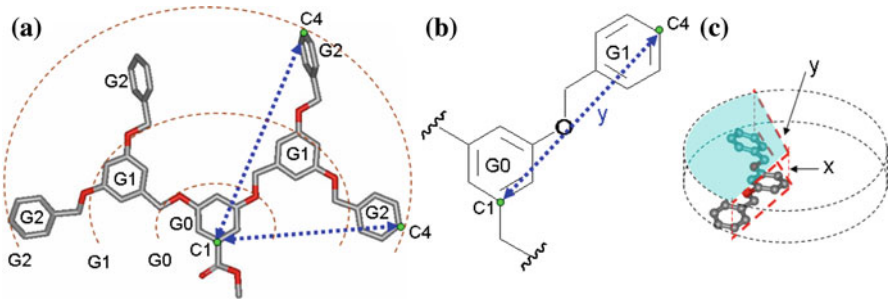

Fig. 4 **a** Distances between C1 atom of the focal G0 phenyl and C4 atoms of G2 phenyl in the structure of which CSD code is RISZIC; **b** the distance (radius) y between the C1 atom of the focal G0 phenyl and the C4 atom of G1 phenyl of a G1 Fréchet-type dendron; **c** for a G1 dendron y is the radius of the cylinder of height x that contains the dendron

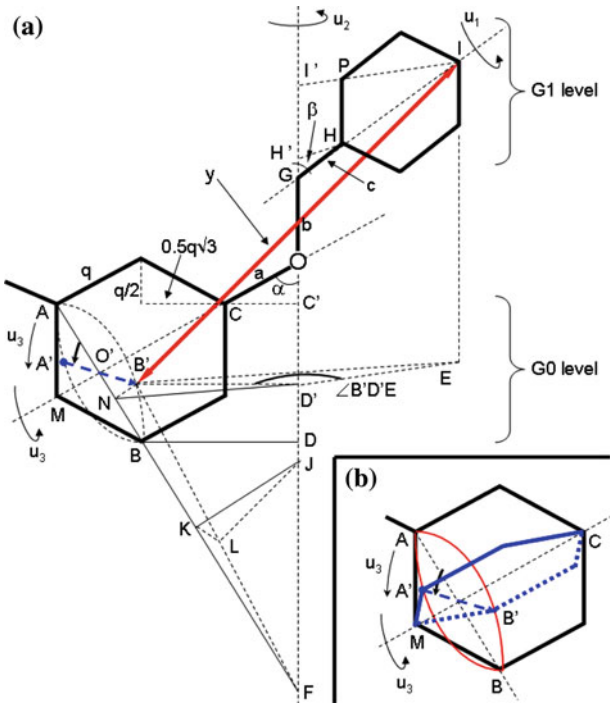

Fig. 5 **a** Geometrical parameters of the distance y = B′I between C1 atom of G0 phenyl and C4 atom of a G1 phenyl (see Fig. 4b); **b** Rotation of G0 phenyl about the CM axis

Let be q = 1.4 Å the average length of the carbon-carbon bond of a phenyl ring. A phenyl ring is considered as a regular hexagon.

A, B, C, M and O′ are in a reference plane that is the plane of the paper (Fig. 5a).

The rotational axis of u_3 is CO or OO′, and the one of u_2 is GO or FI′ (Fig. 5).

The rotation of the G0 phenyl around OO′ generates a circle of center O′. The radius of the rotational circle generated by the rotation of C1 atom of G0 phenyl (i.e. the point B) about the axis OM (or CM or OO′) (Fig. 5a, b), is $A'O = A'O' = B'O' = B'O = 0.5q\sqrt{3} = k_1$. As a consequence of the rotation of the G0 phenyl by the angle u_3 (Fig. 5b), i.e. ∠AO′A′, the points A and B of the plane of the paper are placed in the new positions A′ and B′. B′D′, D′E and II′ are perpendicular to the axis GO (or FI′). D′E = II′, D′E⊥D′I′, B′D′⊥D′I′, D′I|| EI, then EI⊥(B′D′E). B′E ⊂ (B′D′E), so EI ⊥B′E. In the right triangle ΔB′EI:

$$B'I = \left[(B'E)^2 + (EI)^2\right]^{1/2} \tag{8}$$

where

$$(B'E)^2 = (B'D')^2 + (D'E)^2 - 2*B'D'*D'E*\cos(\angle B'D'E) \tag{9}$$

$$EI = D'I' = H'I' + H'G + GO + OC' + C'D'. \tag{10}$$

3.2.1 Calculation of B′E

According to (9) that results from the law of cosines, three elements are required: B′D′, D′E and ∠B′D′E.

3.2.1.1. Calculation of B′D′. In the right triangle ΔB′D′F (B′D′⊥FI′):

$$B'D' = B'F*\sin(B'FD') \tag{11}$$

a. B′F can be calculated in the triangle ΔB′O′F: $B'F^2 = (O'B')^2 + (O'F)^2 - 2*O'B'^*O'F*\cos(\angle B'O'F)$, where $\angle B'O'F = u_3$. To simplify, one may consider $\angle FOO' \approx 60°$, so $\angle O'FO = \angle D'FB = \angle DFB \approx 30°$. AC (not drawn) is parallel to BD, so, as $\angle CAB = 60°$, then $\angle DFB = 30°$ and BF = BD/sin(∠BFD) = $2 * BD = 2(0.5q\sqrt{3}+CC') = q\sqrt{3}+2 * OC * \sin(\angle COC') = q\sqrt{3}+2a*\sin(\alpha)$, where OC = a and $\angle COC' = \alpha$. $O'F = O'B + BF = 1.5q\sqrt{3} + 2a*\sin(\alpha)$. Hence

$$\begin{aligned} B'F^2 = {} & 3q^2/4 + [1.5q\sqrt{3} + 2a*\sin(\alpha)]^2 \\ & -q\sqrt{3}*[1.5q\sqrt{3} + 2a*\sin(\alpha)]*\cos(u_3) \end{aligned} \tag{12}$$

where $3q^2/4 + [1.5q\sqrt{3} + 2a*\sin(\alpha)]^2 = k_2$, $-q\sqrt{3}[1.5q\sqrt{3} + 2a*\sin(\alpha)] = k_3$, then

$$B'F = [k_2 + k_3*\cos(u_3)]^{1/2} \tag{13}$$

b. In order to calculate sin(∠B′FD′), let K be a point on BF, J a point on DF and $\angle JKF = 90°$. ∠DFB = ∠KFJ = 30°, so JK = FJ*sin(∠KFJ) = FJ/2 and

$$FJ = FK/\cos(\angle KFJ) = 2FK/\sqrt{3} \tag{14}$$

Let KL be perpendicular to B′F, so $\angle KLF = 90°$. The plane (BDF) is contained in the plane of the paper. The plane (BB′F) is contained in the plane of the rotational circle that is perpendicular to the plane of the paper. Consequently, (BDF) ⊥ (BB′F). (BDF) ∩ (BB′F) = BF and JK ⊥ BF, then JK ⊥ (BB′F). B′F is contained in the plane (BB′F), so JK ⊥B′F. KL ⊥B′F, so B′F ⊥ (JKL). As LJ⊂(JKL), then JL ⊥B′F. Consequently, $\angle JLF = 90°$ and $\cos(\angle LFJ) = \cos(\angle B'FD') = [1 - \sin^2(\angle LFJ)]^{1/2}$. In the right triangle ΔKFL:

$$FL = FK*\cos(\angle KFL) = FK*[1 - \sin^2(\angle KFL)]^{1/2} \tag{15}$$

Let B′N be perpendicular to O′F. (ABC) ⊥ (ABB′). (ABC)∩(ABB′) = AB, B′N ⊂ (ABB′), B′N ⊥ AB, so B′N ⊥ (ABC). D′N ⊂(ABC), so B′N ⊥D′N. In the triangle ΔFO'B′, the height B′N from B′ is $B'N = O'B'*\sin(u_3)$. So

$\sin(\angle KFL) = \sin(\angle B'FO') = B'N/B'F = O'B'*\sin(u_3)/B'F = 0.5q\sqrt{3}*\sin(u_3)/\{3q^2/4 + [1.5q\sqrt{3} + 2a*\sin(\alpha)]^2 - q(3*[1.5q\sqrt{3} + 2a*\sin(\alpha)]*\cos(u_3)\}^{1/2}$. Hence:

$$\sin(\angle KFL) = k_1*\sin(u_3) / [k_2 + k_3*\cos(u_3)]^{1/2} \tag{16}$$

$\cos(\angle LFJ) = FL/FJ$. From this relation combined with (14) and (15), it results that

$$\cos(\angle LFJ) = \sqrt{3}[1 - \sin^2(\angle KFL)]^{1/2}/2 = \cos(\angle B'FD') \tag{17}$$

$\sin(\angle B'FD') = [1- \cos^2(\angle B'FD')]^{1/2}$. From this relation combined with (17), it results that

$$\sin(\angle B'FD') = \{1 - 3[1 - \sin^2(\angle KFL)]/4\}^{1/2} \tag{18}$$

c. $B'D' = B'F*\sin(\angle B'FD')$. From (11), (12), (13), (16) and (18): $B'D' = \{3q^2/4 + [1.5q\sqrt{3} + 2a*\sin(\alpha)]^2 - q\sqrt{3}[1.5q\sqrt{3} + 2a*\sin(\alpha)]*\cos(u_3)\}^{1/2}*\{1 - 3[1 - 0.75q^2*\sin^2(u_3)/\{3q^2/4 + [1.5q\sqrt{3} + 2a*\sin(\alpha)]^2 - q\sqrt{(3[1.5q\sqrt{3} + 2a*\sin(\alpha)]*\cos(u_3)\}]/4\}^{1/2}$. Hence

$$B'D' = 0.5\left[k_2 + 3k_1^2 + k_3*\cos(u_3) - 3k_1^2\cos^2(u_3)\right]^{1/2} \tag{19}$$

3.2.1.2. Calculation of D′E

$$\begin{aligned} D'E = II' &= IP + I'P = q\sqrt{3} + GH*\sin(\angle HGH') \\ &= q\sqrt{3} + c*\sin(\beta) = k_4 \end{aligned} \tag{20}$$

where GH = c and $\angle HGH' = \beta$.

3.2.1.3. The angles $\angle B'D'E$ and $\angle B'D'N$. The plane of the rotational circle is perpendicular to the plane of the paper. B′N is contained in the plane of the circle and B′N is also perpendicular to O'F. Both O'F and ND' are contained in the plane of the paper, consequently $\angle B'ND' = 90°$, so $\sin(\angle B'D'N) = B'N/B'D'$, and $\angle B'D'N = \arcsin(B'N/B'D')$. $\angle B'D'E = \angle ND'E - \angle B'D'N = u_2 - \angle B'D'N = u_2 - \arcsin(B'N/B'D') = u_2 - \arcsin[0.5q\sqrt{3}*\sin(u_3)/B'D'] = u_2 - \arcsin[k_1*\sin(u_3)/B'D']$.

The angle $\angle B'D'N$ is an acute angle that depends on u_3:

$$\begin{aligned} \angle B'D'N &= \arcsin\left\{2k_1*\sin(u_3)/[-3k_1^2 * \cos^2(u_3) \right. \\ &\qquad \left. + k_3*\cos(u_3) + k_2 + 3k_1^2]^{1/2}\right\} \\ \angle B'D'N &= \arcsin\left\{2.425*\sin(u_3)/[-4.41*\cos^2(u_3) \right. \\ &\qquad \left. -14.695*\cos(u_3) + 42.605]^{1/2}\right\} \end{aligned} \tag{21}$$

$\angle B'D'N$ is comprised between −22.23 and 22.23° (Fig. 6).

3.2.2 Calculation of EI

In the right triangle $\Delta B'D'F$, $D'F = B'F*\cos(\angle B'FD')$. For $\cos(\angle B'FD')$, *vide supra* (17). In the right triangle $\Delta AC'F$, $C'F = AC'/\tan(\angle AFC')$. $\angle AFC' \approx 30°$, so $C'F =$

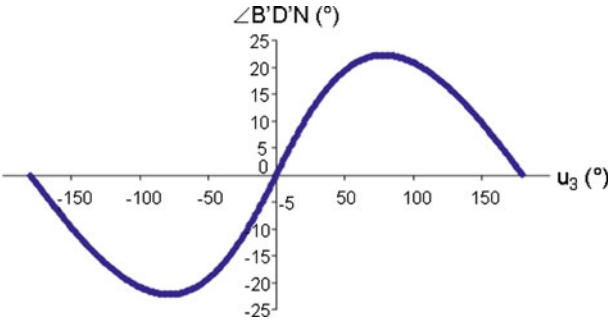

Fig. 6 Dependence of the angle $\angle B'D'N$ on of the torsion angle u_3 for $-180° \leq u_3 \leq 180°$

$AC' * \sqrt{3} = \sqrt{3}[q\sqrt{3} + a * \sin(\alpha)]$. $C'D' = C'F - D'F = \sqrt{3}[q\sqrt{3} + a * \sin(\alpha)] - B'F * \cos(\angle B'FD')$.

$EI = D'I' = H'I' + H'G + GO + OC' + C'D' = q + c * \cos(\beta) + b + a * \cos(\alpha) + \sqrt{3} * [q\sqrt{3} + a * \sin(\alpha)] - \{3q^2/4 + [1.5q\sqrt{3} + 2a * \sin(\alpha)]^2 - q\sqrt{3}[1.5q\sqrt{3} + 2a * \sin(\alpha)] * \cos(u_3)\}^{1/2} * \sqrt{3} * \{1 - 0.75q^2 * \sin^2(u_3)/\{3q^2/4 + [1.5q\sqrt{3} + 2a * \sin(\alpha)]^2 - q\sqrt{3}[1.5q\sqrt{3} + 2a * \sin(\alpha)] * \cos(u_3)\}^{1/2}/2$.

Hence

$$EI = k_5 - 0.5\sqrt{3}\left[k_1^2 * \cos^2(u_3) + k_3 * \cos(u_3) + k_2 - k_1^2\right]^{1/2} \tag{22}$$

For the meaning of k_5, *vide infra*.

3.2.3 All the elements required to calculate $B'I$ as a function of u_2 and u_3 are now known

$$\begin{aligned} y = B'I &= \left[(B'E)^2 + (EI)^2\right]^{1/2} \\ &= \left[(B'D')^2 + (D'E)^2 - 2 * B'D' * D'E * \cos\angle(B'D'E) \right. \\ &\quad \left. + (H'I' + H'G + GO + OC' + C'D')^2\right]^{1/2}. \end{aligned}$$

It results that

$$\begin{aligned} y = \Big\{ & k_3 * \cos(u_3) - k_5 * \sqrt{3}[k_1^2 * \cos^2(u_3) + k_3 * \cos(u_3) - k_1^2 + k_2]^{1/2} \\ & + k_2 + k_4^2 + k_5^2 - k_4 * \Big[-3k_1^2 * \cos^2(u_3) + k_3 \\ & * \cos(u_3) + 3k_1^2 + k_2\Big]^{1/2} * \cos\big[u_2 - \arcsin\{2k_1 * \sin(u_3) \\ & \Big[-3k_1^2 * \cos^2(u_3) + k_3 * \cos(u_3) + 3k_1^2 + k_2\Big]^{1/2}\Big\}\Big]\Big\}^{1/2} \end{aligned} \tag{23}$$

where $k_1 = 0.5q\sqrt{3}$, $k_2 = 3q^2/4 + [1.5q\sqrt{3} + 2a*\sin(\alpha)]^2$, $k_3 = -q\sqrt{3}[1.5q\sqrt{3} + 2a*\sin(\alpha)]$, $k_4 = q\sqrt{3} + c*\sin(\alpha)$, and $k_5 = q + c*\cos(\beta) + b + a*\cos(\alpha) + \sqrt{3}*[q\sqrt{3} + a*\sin(\alpha)]$.

The following values were considered: a = 1.36 Å, b = 1.43 Å, c = 1.54 Å, q = 1.4 Å, $\alpha = 63°$, $\beta = 72°$. The following values were obtained: $k_1 = 1.212$, $k_2 = 38.195$, $k_3 = -14.695$, $k_4 = 3.889$ and $k_5 = 10.223$. k_1, k_2, k_3, k_4 and k_5 are in Å.

$$
\begin{aligned}
y\,(u_2, u_3) = \Big\{ & -14.695*\cos\,(u_3) - 17.707*[1.47*\cos^2\,(u_3) \\
& -14.695*\cos\,(u_3) + 36.725]^{1/2} \\
& +157.834 - 3.889* \Big[-4.41*\cos^2\,(u_3) - 14.695*\cos\,(u_3) + 42.605\Big]^{1/2} * \\
& \cos\Big[u_2 - \arcsin\Big\{2.425*\sin\,(u_3)\,/[-4.41*\cos^2\,(u_3) \\
& -14.695*\cos\,(u_3) + 42.605]^{1/2}\Big\}\Big]\Big\}^{1/2}
\end{aligned}
\tag{24}
$$

For simplification, the distance y has been calculated between two C atoms. The calculations can be adapted in order to take into account the presence of a hydrogen atom or a substituent at the C4 atom.

3.3 Verification

The formula for the calculation of the radius y was applied to a set of values of u_2 and u_3 obtained from published X-ray structures (Table 2): BEQQUK, CAZVAB, EDEWUG, FAVGIT, IXEKIF, LIHPAU, WIBXEL (for references, *vide supra*). The angles and distances were measured through the software Mercury. The average of the differences between calculated and measured values $|y_{calc} - y_{meas}|$ is 0.085 Å. For each measured value, a percentage was calculated with the formula $100*|y_{calc} - y_{meas}|/y_{meas}$; the average of percentages is 1.085%.

3.4 Extrema

With respect to the variable u_2 and to functions $w_i(u_3)$ depending only on u_3, y may be written:

$$
y\,(u_2, u_3) = [w_1 + w_2*\cos\,(u_2 - w_3)]^{1/2} \tag{25}
$$

where

$$
\begin{aligned}
w_1\,(u_3) = & -14.695*\cos\,(u_3) - 17.707*[1.47*\cos^2\,(u_3) - 14.695*\cos\,(u_3) \\
& +36.725]^{1/2} + 157.834 \\
w_2\,(u_3) = & -3.889* \Big[-4.41*\cos^2\,(u_3) - 14.695*\cos\,(u_3) + 42.605\Big]^{1/2}
\end{aligned}
$$

Table 2 Examples of application of the formula for calculation of the distance y

Structure code	u_2 (°)	u_3 (°)	y_{calc} (Å)	y_{meas} (Å)	$\lvert y_{calc} - y_{meas}\rvert$ (Å)	$100*\lvert y_{calc} - y_{meas}\rvert/y_{meas}$
BEQQUK	71.39	−175.06	5.960	6.036	0.076	1.259
	175.14	175.75	8.478	8.447	0.031	0.367
	158.23	174.1	8.346	8.272	0.074	0.895
	171.34	169.32	8.454	8.462	0.008	0.095
	179.5	−0.63	8.727	8.55	0.177	2.070
	−177.82	177.37	8.487	8.454	0.033	0.390
CAZVAB	−177.31	177.94	8.487	8.446	0.041	0.485
EDEWUG	169.77	−177.22	8.466	8.387	0.079	0.942
	−174.21	−8.19	8.712	8.5	0.212	2.494
FAVGIT	177.58	−2.05	8.726	8.558	0.168	1.963
	169.39	−178.87	8.461	8.408	0.053	0.630
IXEKIF	178.45	−177.92	8.487	8.39	0.097	1.156
	−179.57	6.44	8.726	8.562	0.164	1.915
LIHPAU	73.05	−179.9	5.960	6.038	0.078	1.292
	77.36	−168.58	6.288	6.389	0.101	1.581
WIBXEL	−70.15	−175.09	5.779	5.732	0.047	0.820
	78.52	2.59	7.288	7.294	0.006	0.082

$$w_3(u_3) = \arcsin\left\{2.425*\sin(u_3) \Big/ [-4.41*\cos^2(u_3) - 14.695*\cos(u_3) + 42.605]^{1/2}\right\}.$$

Partial differential equations $\partial y/\partial u_2 = 0$ and $\partial y/\partial u_3 = 0$ were solved in order to identify the maxima and minima of $y(u_2,u_3)$.

a. $\partial y/\partial u_2 = 0.5*[-w_2*\sin(u_2 - w_3)]*[w_1 + w_2*\cos(u_2 - w_3)]^{-1/2} = 0$. So $\sin(u_2 - w_3) = 0$. So $u_2 = w_3$ or $u_2 = w_3 \pm 180$.

b. $\partial y/\partial u_3 = 0.5*\left[w_1' + w_2'*\cos(u_2 - w_3) + w_2*w_3'*\sin(u_2 - w_3)\right]*[w_1 + w_2*\cos(u_2 - w_3)]^{-1/2} = 0$.

b.1. If $u_2 = w_3$, then $\partial y/\partial u_3 = 0.5*[w_1' + w_2']*(w_1 + w_2)^{-1/2} = 0$, that is $w_1' + w_2' = 0$.

$$w_1' = 14.695*\sin(u_3) - 0.5*17.707*[-2*1.47*\cos(u_3)*\sin(u_3) + 14.695*\sin(u_3)]*[1.47*\cos^2(u_3) - 14.695*\cos(u_3) + 36.725]^{-1/2}$$

$$w_2' = -0.5*3.889*[4.41*2*\sin(u_3)*\cos(u_3) + 14.695*\sin(u_3)]^{1/2}*[-4.41*\cos^2(u_3) - 14.695*\cos(u_3) + 42.605]^{-1/2}.$$

$$\begin{aligned} w_1{}' + w_2{}' = {} & \sin(u_3) * \{14.695 - 0.5 * 17.707 * [-2 * 1.47 * \cos(u_3) \\ & + 14.695] * [1.47 * \cos^2(u_3) \\ & - 14.695 * \cos(u_3) + 36.725]^{-1/2} \\ & - 0.5 * 3.889 * [4.41 * 2 * \cos(u_3) + 14.695]^{1/2} * [-4.41 * \cos^2(u_3) \\ & - 14.695 * \cos(u_3) + 42.605]^{-1/2}\} = \sin(u_3) * s_1(u_3) = 0 \end{aligned} \tag{26}$$

For the expression of $s_1(u_3)$ *vide infra*.

b.1.1. The above Eq. (26) gives $\sin(u_3) = 0$, therefore $u_3 = 0°$ (and $u_2 = w_3(0°) = 0°$) or $u_3 = \pm 180°$ (and $u_2 = w_3(\pm 180°) = 0°$).

b.1.2. The above Eq. (26) also gives

$$\begin{aligned} s_1(u_3) = {} & \{14.695 - 0.5 * 17.707 * [-2 * 1.47 * \cos(u_3) \\ & + 14.695] * [1.47 * \cos^2(u_3) - 14.695 * \cos(u_3) \\ & + 36.725]^{-1/2} - 0.5 * 3.889 * \\ & [4.41 * 2 * \cos(u_3) + 14.695]^{1/2} * \\ & [-4.41 * \cos^2(u_3) - 14.695 * \cos(u_3) \\ & + 42.605]^{-1/2}\} = 0 \end{aligned} \tag{27}$$

b.2. If $u_2 = w_3 \pm 180°$, then

$$\partial y / \partial u_3 = 0.5 * \left[w_1{}' - w_2{}'\right] * (w_1 - w_2)^{-1/2} = 0 \tag{28}$$

that is

$$\begin{aligned} w_1{}' - w_2{}' = {} & \sin(u_3) * \{14.695 - 0.5 * 17.707 * [-2 * 1.47 * \cos(u_3) \\ & + 14.695] * [1.47 * \cos^2(u_3) - 14.695 * \cos(u_3) + 36.725]^{-1/2} \\ & + 0.5 * 3.889 * [4.41 * 2 * \cos(u_3) + 14.695]^{1/2} * [-4.41 * \cos^2(u_3) \\ & - 14.695 * \cos(u_3) + 42.605]^{-1/2}\} = \sin(u_3) * s_2(u_3) = 0 \end{aligned} \tag{29}$$

For the expression of $s_2(u_3)$ *vide infra*.

b.2.1. The above Eq. (29) gives $\sin(u_3) = 0$, therefore $u_3 = 0°$ (and $u_2 = \pm 180°$) or $u_3 = \pm 180°$ (and $u_2 = \pm 180°$).

b.2.2. The above Eq. (29) also gives

$$\begin{aligned} s_2(u_3) = {} & \{14.695 - 0.5 * 17.707 * [-2 * 1.47 * \cos(u_3) + 14.695] \\ & * [1.47 * \cos^2(u_3) - 14.695 * \cos(u_3) + 36.725]^{-1/2} \\ & + 0.5 * 3.889 * [4.41 * 2 * \cos(u_3) + 14.695]^{1/2} * \\ & [-4.41 * \cos^2(u_3) - 14.695 * \cos(u_3) + 42.605]^{-1/2}\} = 0 \end{aligned} \tag{30}$$

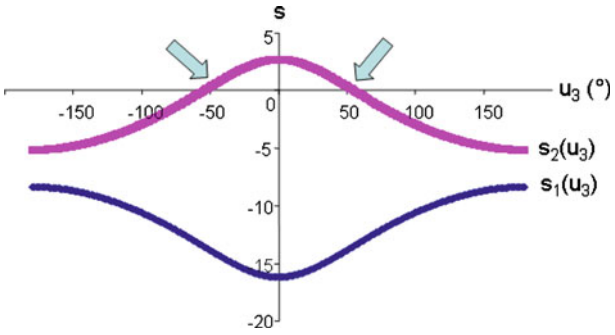

Fig. 7 Representation of functions $s_1(u_3)$ and $s_2(u_3)$ for $-180 \leq u_3 \leq 180°$

b.3. Both equations $s_1(u_3) = 0$ (27) and $s_2(u_3) = 0$ (30) were solved through a graphical method, by representing $s_1(u_3)$ and $s_2(u_3)$ as a function of u_3 and finding its intersections with x axis (Fig. 7).

b.3.1. As it can be seen (Fig. 7), $s_1(u_3) \neq 0$ for $-180° \leq u_3 \leq 180°$.

b.3.2. $s_2(-54.2°) = s_2(54.2°) = 0.000441$ (Fig. 7), so $u_3 = \pm 54.2°$ can be considered as a good approximation of the solution of the equation $s_2(u_3) = 0$. $w_3(54.2°) = 20.19$ and $w_3(-54.2°) = -20.19$. But $u_2 = w_3 \pm 180°$ and $-180° \leq u_2 \leq 180°$, so: $u_2 = -159.81°$ for $u_3 = 54.2°$, and $u_2 = 159.81°$ for $u_3 = -54.2°$.

c. Hence, the following extrema were found: a) $y(0°, 0°) = 6.20$ Å, b) $y(\pm 180°, 0°) = 8.73$ Å, c) $y(0°, \pm 180°) = 3.93$Å, d) $y(\pm 180°, \pm 180°) = 8.45$Å, and e) $y(-159.81°, 54.2°) = y(159.81°, -54.2°) = 8.76$Å.

3.5 Application

The volume v of a G1 dendron as a function of the conformation (angles u_2 and u_3) can be evaluated in the following way. One may consider that y is the radius of the cylinder of height x that is generated by the dendron and contains it (Fig. 4c). Of this cylinder, only a percentage p is occupied by the dendron. Then, the volume is $v(u_2, u_3) = \pi * y^2(u_2, u_3) * x * p$.

4 Conclusions and perspectives

A geometrical approach to two important distances in Fréchet-type dendrimers was presented in this work, namely (i) the dependence of the distance between the centres of the two phenyl rings of a benzyl-phenyl-ether motif on the conformation, and (ii) the calculation of the radius of a G1 dendron (i.e. the distance between the C1 atom of the focal phenyl ring and the C4 atom of a superior phenyl). This approach results in the mathematical expression of these distances as a function of the torsion angles

on which they depend. The expression of y shows that the radius of a G1 dendron depends on angles u_2 and u_3 following a quite complex relation.

Comparison of calculated values with the values observed in X-ray structures shows good agreement between calculated and experimentally measured values. Several approximations and simplifications were done and average values of bonds and angles were considered for these calculations. These approximations may produce more or less important differences between calculated and measured values.

The distance y has been calculated as a distance between two C atoms. The calculations can be adapted in order to take into account the presence of a hydrogen atom or a substituent at the C4 atom.

This approach enabled determination of the extreme values of these distances.

As a perspective, in spite of the complexity of these calculations, it would be interesting to deduce the mathematical relation between the C4 atom of termini phenyl rings and the C1 atom of the focal phenyl ring in higher generation dendrimers, like G2 and G3.

References

1. S. Gestermann, R. Hesse, B. Windisch, F. Vögtle, in *Stimulating Concepts in Chemistry*, ed. by F. Vögtle, J.F. Stoddart, M. Shibasaki (Wiley, Weinheim, 2000) pp. 187–198
2. G.R. Newkome, C. Moorefield, F. Vögtle, *Dendrimers and Dendrons* (Wiley, New York, 2001)
3. J.M.J. Fréchet, D.A Tomalia (ed.), *Dendrimers and Other Dendritic Polymers* (Wiley, Weinheim, 2001)
4. S. Hecht, J. Polym. Sci. Part A **41**, 1047–1058 (2003)
5. J.N.H. Reek, S. Arévalo, R. van Heerbeek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Adv. Catal. **49**, 71–151 (2006)
6. F. Vögtle, G. Richardt, N. Werner, *Dendrimer Chemistry* (Wiley, New York, 2009)
7. A. Carlmark, C. Hawker, A. Hulta, M. Malkoch, Chem. Soc. Rev. **38**, 352–362 (2009)
8. O. Rolland, C.-O. Turrin, A.-M. Caminade, J.-P. Majoral, New J. Chem. **33**, 1809–1824 (2009)
9. R.K. Tekade, P.V. Kumar, N.K. Jain, Chem. Rev. **109**, 49–87 (2009)
10. C. Dufès, I.F. Uchegbu, A.G. Schätzlein, Adv. Drug Deliv. Rev. **57**, 2177–2202 (2005)
11. D.J. Coles, I. Toth, Curr. Drug Deliv. **6**, 338–342 (2009)
12. T.A. Theodossiou, A. Pantos, I. Tsogas, C.M. Paleos, Chem. Med. Chem. **3**, 1635–1643 (2008)
13. M. Guillot-Nieckowski, S. Eisler, F. Diederich, New J. Chem. **31**, 1111–1127 (2007)
14. U. Boas, P.M.H. Heergaard, Chem. Soc. Rev. **33**, 43–63 (2004)
15. S.H. Medina, M.E.H. El-Sayed, Chem. Rev. **109**, 3141–3157 (2009)
16. Y. Cheng, T. Xu, Eur. J. Medi. Chem. **43**, 2291–2297 (2008)
17. Y. Cheng, Z. Xu, M. Ma, T. Xu, J. Pharm. Sci. **97**, 123–143 (2008)
18. D. Astruc, F. Chardac, Chem. Rev. **101**, 2991–3024 (2001)
19. G.E. Oosterom, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Angew. Chem. Int. Ed. **40**, 1828–1849 (2001)
20. Y.-M. Chung, H.-K. Rhee, Korean J. Chem. Eng. **21**, 81–97 (2004)
21. D. Méry, D. Astruc, Coord. Chem. Rev. **250**, 1965–1979 (2006)
22. L.H. Gade (ed.), *Dendrimer Catalysis* (Springer, Berlin, 2006)
23. G.R. Newkome, K.S. Yoo, S.-H. Hwang, C.N. Moorefield, Tetrahedron **59**, 3955–3964 (2003)
24. M. Higuchi, A. Hayashi, D.G. Kurth, J. Nanosci. Nanotechnol. **6**, 1533–1551 (2006)
25. Y. Tor, C. R. Chimie **6**, 755–766 (2003)
26. E. Constable, Chem. Commun. 1073–1080 (1997)
27. S.-H. Hwang, C.D. Shreiner, C.N. Moorefield, G.R. Newkome, New J. Chem. **31**, 1192–1217 (2007)
28. V. Balzani, G. Bergamini, P. Ceroni, F. Vögtle, Coord. Chem. Rev. **251**, 525–535 (2007)
29. S.-H. Hwang, C.N. Moorefield, G.R. Newkome, Chem. Soc. Rev. **37**, 2543–2557 (2008)
30. S.-C. Lo, P.L. Burn, Chem. Rev. **107**, 1097–1116 (2007)
31. A.M. Naylor, W.A. Goddard III, G.E. Kiefer, D.A. Tomalia, J. Am. Chem. Soc. **111**, 2339–2341 (1989)

32. R. Scherrenberg, B. Coussens, P. van Vliet, G. Edouard, J. Brackman, E. de Brabander, K. Mortensen, Macromolecules **31**, 456–461 (1998)
33. T. Zhou, C.S. Bor, Macromolecules **38**, 8554–8561 (2005)
34. P. Welch, M. Muthukumar, Macromolecules **31**, 5892–5897 (1998)
35. E.G. Timoshenko, Y.A. Kuznetsov, R. Connolly, J. Chem. Phys. **117**, 9050–9062 (2002)
36. M. Ballauff, C.N. Likos, Angew. Chem. Int. Ed. **43**, 2998–3020 (2004)
37. T. Hong, H.-I. Kim, Macromol. Res. **12**, 178–188 (2004)
38. W. Ortiz, A.E. Roitberg, J.L. Krause, J. Phys. Chem. B **108**, 8218–8225 (2004)
39. K. Karatasos, D.B. Adolf, G.R. Davies, J. Chem. Phys. **115**, 5310–5318 (2001)
40. K.L. Wooley, C.A. Klug, K. Tasaki, J. Schaefer, J. Am. Chem. Soc. **119**, 53–58 (1997)
41. C.B. Gorman, M.W. Hager, B.L. Parkhurst, J.C. Smith, Macromolecules **31**, 815–822 (1998)
42. C.J. Hawker, K.L. Wooley, J.M.J. Fréchet, J. Am. Chem. Soc. **115**, 4375–4376 (1993)
43. S. De Backer, Y. Prinzie, W. Verheijen, M. Smet, K. Desmedt, W. Dehaen, F.C. De Schryver, J. Phys. Chem. A **102**, 5451–5455 (1998)
44. T.H. Mourey, S.R. Turner, M. Rubinstein, J.M.J. Fréchet, C.J. Hawker, K.L. Wooley, Macromolecules **25**, 2401–2406 (1992)
45. C.J. Hawker, J.M.J. Fréchet, J. Am. Chem. Soc. **112**, 7638–7647 (1990)
46. C.J. Hawker, J.M.J. Fréchet, Macromolecules **23**, 4726–4729 (1990)
47. C.J. Hawker, J.M.J. Fréchet, J. Chem. Soc., Chem. Commun. **1990**, 1010–1013 (1990)
48. S.M. Grayson, J.M.J. Fréchet, Chem. Rev. **101**, 3819–3868 (2001)
49. S.C. Zimmerman, M.S. Wendland, N.A. Rakow, I. Zharov, K.S. Suslick, Nature **418**, 399–403 (2002)
50. H.-F. Chow, I.Y.-K. Chan, C.C. Mak, Tetrahedron Lett. **36**, 8633–8636 (1995)
51. H.-F. Chow, I.Y.-K. Chan, C.C. Mak, M.-K. Ng, Tetrahedron **52**, 4277–4290 (1996)
52. C.C. Mak, H.-F. Chow, Macromolecules **30**, 1228–1230 (1997)
53. N. Nishiyama, H.R. Stapert, G.-D. Zhang, D. Takasu, D.-L. Jiang, T. Nagano, T. Aida, K. Kataoka, Bioconj. Chem. **14**, 58–66 (2003)
54. M. Malkoch, K. Schleicher, E. Drockenmuller, C.J. Hawker, T.P. Russell, P. Wu, V.V. Fokin, Macromolecules **38**, 3663–3678 (2005)
55. A.-M. Stadler, L. Brelot, Cryst. Growth Des. **10**, 2285–2290 (2010)
56. G.M. Hübner, G. Nachtsheim, Q.Y. Li, C. Seel, F. Vögtle, Angew. Chem. Int. Ed. **39**, 1269–1272 (2000)
57. V. Percec, B.C. Won, M. Peterca, P.A. Heiney, J. Am. Chem. Soc. **129**, 11265–11278 (2007)
58. V. Percec, W.-D. Cho, G. Ungar, J. Am. Chem. Soc. **122**, 10273–10281 (2000)
59. V. Percec, M.R. Imam, M. Peterca, D.A. Wilson, R. Graf, H.W. Spiess, V.S.K. Balagurusamy, P.A. Heiney, J. Am. Chem. Soc. **131**, 7662–7677 (2009)
60. V. Percec, M.R. Imam, M. Peterca, D.A. Wilson, P.A. Heiney, J. Am. Chem. Soc. **131**, 1294–1304 (2009)
61. K.J. Naidoo, S.J. Hughes, J.R. Moss, Macromolecules **32**, 331–341 (1999)
62. O. Lukin, D. Schubert, C.M. Müller, W.B. Schweizer, V. Gramlich, J. Schneider, G. Dolgonos, A. Shivanyuk, Proc. Nat. Acad. Sci. **106**, 10922–10927 (2009)
63. E.C. Constable, B.A. Hermann, C.E. Housecroft, L. Merz, L.J. Scherer, Chem. Commun. 928–929 (2004)
64. L.J. Scherer, L. Merz, E.C. Constable, C.E. Housecroft, M. Neuburger, B.A. Hermann, J. Am. Chem. Soc. **127**, 4033–4041 (2005)
65. L. Merz, H.-J. Güntherodt, L.J. Scherer, E.C. Constable, C.E. Housecroft, B.A. Hermann, Chem.–Eur. J. **11**, 2307–2318 (2005)
66. Z. Pan, E.Y. Cheung, K.D.M. Harris, E.C. Constable, C.E. Housecroft, Cryst. Grow. Des. **4**, 451–455 (2004)
67. Z. Pan, E.Y. Cheung, K.D.M. Harris, E.C. Constable, C.E. Housecroft, Cryst. Grow. Des. **5**, 2084–2090 (2005)
68. G.M. Crippen, J. Math. Chem. **6**, 307–324 (1991)
69. G. Del Río Echenique, R. Rodríguez Schmidt, J.J. Freire, J.G. Hernández Cifre, J. García de la Torre, J. Am. Chem. Soc. **131**, 8548–8556 (2009)
70. J.G. Speight, *Perry's Standard Tables and Formulas for Chemical Engineers* (McGraw-Hill, New York, 2003), p. 32
71. R.W. Saalfrank, C. Deutscher, H. Maid, A.M. Ako, S. Sperner, T. Nakajima, W. Bauer, F. Hampel, B.A. Heß, N.J.R. van Eikema Hommes, R. Puchta, F.W. Heinemann, Chem. Eur. J. **10**, 1899–1905 (2004)

72. E.C. Constable, B.A. Hermann, C.E. Housecroft, M. Neuburger, S. Schaffner, L.J. Scherer, New J. Chem. **29**, 1475–1481 (2005)
73. W.-Z. Chen, P.E. Fanwick, T. Ren, Inorg. Chem. **46**, 3429–3431 (2007)
74. D. Pawlica, M. Marszałek, G. Mynarczuk, L. Sieroń, J. Eilmes, New J. Chem. **28**, 1615–1621 (2004)
75. T. Gibtner, F. Hampel, J.-P. Gisselbrecht, A. Hirsch, Chem. Eur. J. **8**, 408–432 (2002)
76. A. Sánchez-Méndez, E. de Jesús, J.C. Flores, P. Gómez-Sal, Inorg. Chem. **46**, 4793–4795 (2007)
77. H.-B. Yang, A.M. Hawkridge, S.D. Huang, N. Das, S.D. Bunge, D.C. Muddiman, P.J. Stang, J. Am. Chem. Soc. **129**, 2120–2129 (2007)
78. B. Karakaya, W. Claussen, K. Gessler, W. Saenger, A.-D. Schlüter, J. Am. Chem. Soc. **119**, 3296–3301 (1997)