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TOPOLOGICAL SYMMETRY OF TWO FAMILIES OF DENDRIMERS

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ABSTRACT. A dendrimer is an artificially manufactured or synthesized molecule built up from branched units called monomers. In this paper, the mathematical tools of group theory have been used extensively for the analysis of the symmetry properties of these macromolecules. We prove that it is possible to write the symmetry of a dendrimer, as wreath product of some finite groups. To prove, we consider two infinite classes of dendrimers and compute their topological symmetry groups.

Keywords: *Symmetry group, dendrimer, wreath product.*

INTRODUCTION

Dendrimers are one of the main objects of nanobiotechnology. They possess a well defined molecular topology. Their step-wise growth follows a mathematical progression. In an exact phrase, dendrimers are hyperbranched macromolecules, showing a rigorous, aesthetically appealing architecture [1-3].

Group theory is one of the most important branches of mathematics for studying molecular structures of compounds. By using tools taken from the group theory, it is possible to evaluate chemical structures according to their symmetry. Here, by symmetry of a molecule, we mean the automorphism group symmetry of its molecular graph. This type of symmetry also called a topological symmetry, accounts only for the bond relations between atoms, and does not fully determine the molecular geometry. The symmetry of a molecular graph does not need to be the same as (i.e. isomorphic to) the molecular point group symmetry. However, it does represent the maximal symmetry which the geometrical realization of a given topological structure may posses [4].

We first recall some algebraic definitions that will be used in the paper. The symmetry of a physical object can be formalized by the notion of a group action: every element of the group "acts" like a bijective map on some set. To clarify this notion, we assume that G is a group and X is a set.

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G is said to act on X when there is a map $\phi : G \times X \longrightarrow X$ such that for all elements $x \in X$, (i) $\phi(e,x) = x$ where e is the identity element of G, and, (ii) $\phi(g, \phi(h,x)) = \phi(gh,x)$ for all $g,h \in G$. In this case, G is called a transformation group; X is called a G-set, and ϕ is called the group action. For simplicity we define $gx = \phi(g,x)$. In a group action, a group permutes the elements of X. The identity does nothing, while a composition of actions corresponds to the action of the composition. For a given X, the set $\{gx \mid g \in G\}$, where the group action moves *x*, is called the group orbit of *x*. The subgroup which fixes is the isotropy group of *x*.

Let G be a group and N be a subgroup of G. N is called a *normal subgroup* of G, if for any $g \in G$ and $x \in N$, $g^{-1}xg \in N$. Moreover, if H is another subgroup of G such that $H \cap N = \{e\}$ and $G = HN = \{xy \mid x \in H, y \in N\}$, then we say that G is a semidirect product of H by N denoted by $H \wedge N$. Suppose X is a set. The set of all permutations on X, denoted by S_X, is a group which is called the symmetric group on X. In the case that $X = \{1, 2, \ldots, n\}$, we denote S_X by S_n or Sym(n).

Let H be a permutation group on X, a subgroup of S_X, and let G be a group. The set of all mappings $X \longrightarrow G$ is denoted by G^X, i.e. $G^X = \{f \mid f: X \longrightarrow G\}$. It is clear that $|G^X| = |G|^{|X|}$. We put $G \wr H = G^X \times H = \{(f; \pi) \mid f \in G^X, \pi \in H\}$. For $f \in G^X$ and $\pi \in H$, we define $f_\pi \in G^X$ by $f_\pi = f o \pi^{-1}$, where "o" denotes the composition of functions. It is easy to check that the composition law $(f ; \pi) (f' ; \pi') = (ff'_\pi ; \pi \pi')$, makes $G \wr H$ into a group. This group is called the wreath product of G by H [5]. In some leading papers, Balasubramanian [6–13] introduced the wreath product formalism for computing symmetry of molecules. The present authors continued the mentioned works [14-27] to present a computational approach which is valuable in practical problems. Our calculation within the paper was done by the computer algebra system GAP [28], which is freely accessible from internet.

RESULTS AND DISCUSSION

In this section, we describe our computational approach by GAP in computing symmetry of dendrimer, Figure 1. This method is appropriate for molecules which consist of a number of XY_2 or XY_3 groups (as CH_3 or NO_2) attached to a rigid framework. An Example of such molecule is a dendrimer, which is considered here in some detail, see Figures 1 and 2. With a geometric consideration of dynamic symmetries of the molecules we will show that the symmetry group of the molecule can be specified by wreath product of some known groups. Then based on the structure of the group we apply GAP as a useful package for computing the generating set and also the group structure of this molecule.

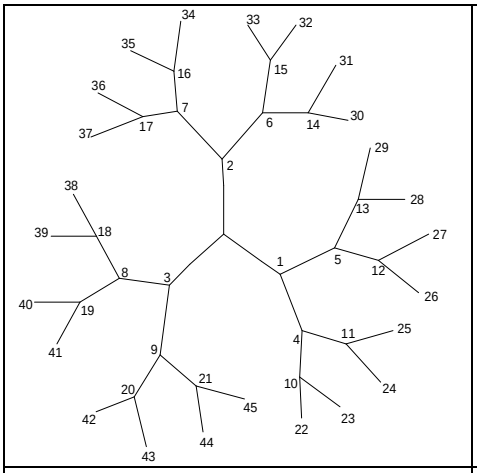

Figure 1. The Forth Generation of Dendrimer Molecule $D_1[4]$.

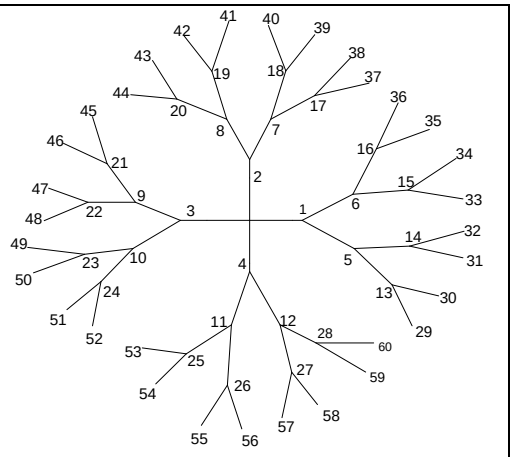

Figure 2. The Forth Generation of Dendrimer Molecule $D_2[4]$.

At first, we consider the dendrimer molecule $D_1[n]$, Figure 1. In order to characterize the symmetry of this molecule we note that each dynamic symmetry operation of $D_1[1]$, considering the rotations of XY_2 groups in different generations of the whole molecule $D_1[n]$, is composed of n sequential physical operations. We first have a physical symmetry of the framework (as we have to map the XY_2 groups on XY_2 groups which are on vertices of the framework). Such operations form the group G of order 6, which as is well known to be isomorphic to S_3 or Sym(3). After accomplishing the first framework symmetry operation we have to map each of the three XY_2 group on itself in the first generation and so on. This is a group isomorphic to $H = ((\ldots(Z_2 \wr Z_2) \wr Z_2) \wr \ldots) \wr Z_2) \wr Z_2$ with n – 1 components. Therefore, the whole symmetry group is isomorphic to $H \wr G$. This is a group of order $6 \times (2^{3(2^{n-1}-1)})$.

We now compute a generator set for this group. To do this, we apply computer algebra system GAP to find a generating set for $D_1[2]$, $D_1[3]$ and $D_1[4]$, see Table 1.

Table 1. Generating Sets for $D_1[2]$, $D_1[3]$ and $D_1[4]$.

a_1 = (1,2)	**a_2 = (1,2,3)**	**b_1 = (4,5)**	**b_2 = (6,7)**	**b_3 = (8,9)**	**b_4 = (10,11)**
b_5 = (12,13)	**b_6 = (14,15)**	**b_7 = (16,17)**	**b_8 = (18,19)**	**b_9 = (20,21)**	**b_{10} = (22,23)**
b_{11} = (24,25)	**b_{12} = (26,27)**	**b_{13} = (28,29)**	**b_{14} = (30,31)**	**b_{15} = (32,33)**	**b_{16} = (34,35)**
b_{17} = (36,37)	**b_{18} = (38,39)**	**b_{19} = (40,41)**	**b_{20} = (42,43)**	**b_{21} = (44,45)**	

Suppose $B_1 = \{a_1 , a_2\}$, $B_2 = \{b_1 , b_2 , b_3\}$, $B_3 = \{b_4 , b_5 , b_6 , b_7 , b_8 , b_9\}$ and $B_4 = \{b_{10} , b_{11} , b_{12} , b_{13} , b_{14} , b_{15} , b_{16} , b_{17} , b_{18} , b_{19} , b_{20} , b_{21}\}$. Then $B_1 \cup B_2$, $B_1 \cup B_2 \cup B_3$ and $B_1 \cup B_2 \cup B_3 \cup B_4$ are generating sets of the topological symmetry of $D_1[2]$, $D_1[3]$ and $D_1[4]$. From these calculations, we define permutations $b_{3(2^{i-2}-1)+1}$ and $b_{3(2^{i-2}-1)}$, $2 \le i \le n$, as follows:

$$b_{3(2^{i-2}-1)+1} = \left(3\left(2^{i-1}-1\right)+1 , 3\left(2^{i-1}-1\right)+2\right) b_{3(2^{i-2}-1)} = \left(3\left(2^{i}-1\right)-1 \ , \ 3\left(2^{i}-1\right)\right)$$

.

Then $B_1 \cup B_2 \cup B_3 \cup \ldots \cup B_n$ is a generating set for $D_1[n]$, where $B_i = \{b_{3(2^{i-2}-1)+1}, \ldots, b_{3(2^{i-2}-1)}\}$.

We now consider the dendrimer molecule $D_2[n]$, Figure 2. The topological symmetry group of the core of this dendrimer is isomorphic to S_4. This group can be generated by $a_1 = (1,2)$, $a_2 = (1,3)$ and $a_3 = (1,4)$. In order to characterize the symmetry of this molecule we note that each dynamic symmetry operation of $D_2[n]$, considering the rotations of XY_2 groups in different generations of the whole molecule $D_2[n]$, is composed of n sequential physical operations. We first have a physical symmetry of the framework (as we have to map the XY_2 groups on XY_2 groups which are on vertices of the framework). Such operations form the group G of order 24, which as is well known to be isomorphic to S_4 or Sym(4). After accomplishing the first framework symmetry operation we have to map each of the four XY_2 group on itself in the first generation and so on. This is a group isomorphic to $H = ((\ldots(Z_2 \wr Z_2) \wr Z_2) \wr \ldots)\wr Z_2) \wr Z_2$ with n – 1 components. Therefore, the whole symmetry group is isomorphic to $H \wr G$. This is a group of order $24 \times 2^{(2^{n+1}-4)}$.

Suppose $B_1 = \{a_1 , a_2 , a_3\}$, $B_2 = \{b_1 , b_2 , b_3 , b_4\}$, $B_3 = \{b_5 , b_6 , b_7 , b_8 , b_9\ b_{10} , b_{11} , b_{12}\}$ and $B_4 = \{b_{13} , b_{14} , b_{15} , b_{16} , b_{17} , b_{18} , b_{19} , b_{20} , b_{21}, b_{22} , b_{23} , b_{24} , b_{25} , b_{26} , b_{27} , b_{28}\}$, where b_i's are defined as follows:

Table 2. Generating Sets for $D_2[2]$, $D_2[3]$ and $D_2[4]$.

b_1 = (5,6)	**b_2 = (7,8)**	**b_3 = (9,10)**	**b_4 = (11,12)**	**b_5 = (13,14)**	**b_6 = (15,16)**
b_7 = (17,18)	**b_8 = (19,20)**	**b_9 = (21,22)**	**b_{10} = (23,24)**	**b_{11} = (25,26)**	**b_{12} = (27,28)**
b_{13} = (29,30)	**b_{14} = (31,32)**	**b_{15} = (33,34)**	**b_{16} = (35,36)**	**b_{17} = (37,38)**	**b_{18} = (39,40)**
b_{19} = (41,42)	**b_{20} = (43,44)**	**b_{21} = (45,46)**	**b_{22} = (47,48)**	**b_{23} = (49,50)**	**b_{24} = (51,52)**
b_{25} = (53,54)	**b_{26} = (55,56)**	**b_{27} = (57,58)**	**b_{28} = (59,60)**		

Then $B_1 \cup B_2$, $B_1 \cup B_2 \cup B_3$ and $B_1 \cup B_2 \cup B_3 \cup B_4$ are generating sets of the topological symmetry of $D_2[2]$, $D_2[3]$ and $D_2[4]$. From these calculations, we define two permutations $b_{4(2^{i-2}-1)+1}$ and $b_{4(2^{i-1}-1)}$, $2 \le i \le n$, as follows:

$$b_{4(2^{i-2}-1)+1} = \left(4\left(2^{i-1}-1\right)+1\ ,\ 4\left(2^{i-1}-1\right)+2\right),$$
$$b_{4(2^{i-1}-1)} = \left(4\left(2^{i}-1\right)-1\ ,\ 4\left(2^{i}-1\right)\right).$$

Then $B_1 \cup B_2 \cup B_3 \cup \ldots \cup B_n$ is a generating set for $D_2[n]$, where $B_i = \{b_{4(2^{i-2}-1)+1}, \ldots, b_{4(2^{i-1}-1)}\}$.

CONCLUSIONS

In this paper a general method for computing symmetry of a molecule is presented, which is useful for hyperbranched compounds. We apply our method for two different types of dendrimers and proved that the symmetry groups of these molecules can be reformulated as wreath product of a sequence of well-known finite groups. Using computer algebra system GAP the generating sets for these classes of dendrimers were computed. Our method is general and can be applied to other dendrimers and nanostars.

REFERENCES

1. F. Isaure, P. A. G. Cormack, D. C. Sherrington, *Reactive & Functional Polymers*, **2006,** *66*, 65.
2. H. Meier, M. Lehmann, *Angew. Chem. Int. Ed.*, **1998**, 37, 643.
3. N. C. Beck Tan, L. Balogh, S. F. Trevino, D. A. Tomali, J. S. Lin, *Polymer*, **1999,** *40***,** 2537.
4. G. S. Ezra, *Symmetry Properties of Molecules*, Lecture Notes in Chemistry 28, Springer, **1982**.
5. D. J. S. Robinson, *A course in the theory of groups*, Second edition. Springer-Verlag, New York, **1996**.
6. K. Balasubramanian, *Journal of Chemical Physics*, **1980**, 72, 665.
7. K. Balasubramanian, *Journal of Chemical Physics*, **1981**, *75*, 4572.
8. K. Balasubramanian, *Studies in Physical Theoretical Chemistry*, **1983**, *23*, 149.
9. X. Y. Liu, K. Balasubramanian, *Journal of Computational Chemistry*, **1990**, *11*, 589.
10. K. Balasubramanian, *Theoretica Chimica Acta*, **1990**, *78*, 31.

11. K. Balasubramanian, *Journal of Physical Chemistry*, **2004**, *108*, 5527.
12. K. Balasubramanian, *Chemical Physics Letters*, **2004**, *391*, 64.
13. K. Balasubramanian, *Chemical Physics Letters*, **2004**, *398*, 15.
14. A.R. Ashrafi, M. Hamadanian, *Croatica Chemica Acta*, **2003**, *76*, 299.
15. M. Hamadanian, A.R. Ashrafi, *Croatica Chemica Acta*, **2003**, *76*, 305.
16. A. R. Ashrafi, *MATCH - Communications in Mathematical and in Computer Chemistry*, **2005**, *53*, 161.
17. A. R. Ashrafi, *Chemical Physics Letters*, **2005**, *403*, 75.
18. M.R. Darafsheh, Y. Farjami, A.R. Ashrafi, *MATCH - Communications in Mathematical and in Computer Chemistry*, **2005**, *54*, 53.
19. M. R. Darafsheh, Y. Farjami, A. R. Ashrafi, *Bulletin of the Chemical Society of Japan*, **2005**, *78*, 996.
20. M. R. Darafsheh, A. R. Ashrafi, A. Darafsheh, *International Journal of Quantum Chemistry,* **2005**, *105*, 485.
21. M. R. Darafsheh, A. R. Ashrafi, A. Darafsheh, *Acta Chimica Slovenica,* **2005**, *52*, 282.
22. M.R. Darafsheh, A.R. Ashrafi, A. Darafsheh, *Chemical Physics Letters*, **2006**, *421*, 566.
23. M. R. Darafsheh, A.R. Ashrafi, A. Darafsheh, *International Journal of Quantum Chemistry*, **2007**, *107*, 340.
24. M.R. Darafsheh, Y. Farjami, A.R. Ashrafi, M. Hamadanian, *J. Math. Chem.,* **2007**, *41*, 315.
25. M.R. Darafsheh, Y. Farjami, A.R. Ashrafi, *MATCH - Communications in Mathematical and in Computer Chemistry*,**2005**, *54*, 331.
26. M. R. Darafsheh, A. R. Ashrafi, A. Darafsheh, *MATCH Commun Math Comput Chem*., **2007**, *58*, 47.
27. M. R. Darafsheh, A. R. Ashrafi, A. Darafsheh, *International Journal of Quantum Chem*istry, **2008**, *108*, 440.

The GAP Team, GAP, Groups, Algorithms and Programming, Lehrstuhl De für Mathematik, RWTH, Aachen, **1995**.