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Computational determination of character table and symmetry of fullerenes cage as C_{24} and C_{28}

Mahboube Eslami Moghadam[a,*], Abdolghafar Abolhosseini Shahrnoy[b], Taghi Karimi[c], Satar Alyar[d]

[a]*Chemistry and Chemical Engineering Research Center of Iran, Tehran, Iran*

[b]*Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, Tehran 14115-175, Iran*

[c]*Department of Mathematics, Payame Noor University, P.O.BOX 19395-3697, Tehran, Iran*

[d]*Department of Mathematics, Azad University, Bonab Branch, Bonab, Iran*

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Abstract

Fullerene chemistry is nowadays a well-established field of both theoretical and experimental investigations. This study considers the symmetry of small fullerenes cage C_{24} and C_{28}. Using PM3 program for C_{24} and C_{28} fullerenes, O_h and T_d symmetry were confirmed, respectively. The mentioned algorithm to compute the automorphism group of these fullerenes with connectivity and geometry of their symmetry point groupswas improved . Here, we computedthe symmetry of these small fullerenes by simple method such as Groups, Algorithms and Programming (GAP) system. It was proved that there are groups of order 48 which has 10 conjugacy classes for C_{24} and 24 which has 5 conjugacy classes for C_{28}, respectively. t ,Alsohe conjugacy classes and character table were computed.

Keywords: Character table, fullerene, symmetry, GAP, hyperchem.

Introduction

Group theory is the mathematics of symmetries and plays an important role in the study of molecules, crystals, and clusters in chemistry although applications have usually been restricted to small or moderately sized

*Corresponding author: Mahboube Eslami Moghadam
Tel: +98 (21) 44787772, Fax: +98 (21) 44787753
E-mail: eslami_moghadam@ccerci.ac.ir; eslami_moghadam@yahoo.com

systems due to computational limitations. To be practical for large systems, finite group theory requires both computer calculation and the advanced computational methods. Group theory for non-rigid molecules is more relevant to large amplitude motion of molecules and its applications appear in the literature [1-5].

Because of their distinctive properties, fullerenes have experienced a tremendous amount of research interest. Fullerenes are very useful candidates for the synthesis of these new materials, and have been extensively studied for a decade [6]. All the fullerenes smaller than C_{60}, C_{36} and C_{28}, C_{24} and C_{20} are found in 1988 [7], 1992 [8], 1998 [9] and 2000 [10], respectively. An explosive growth in fullerene research was triggered in 1990 by the development of a method to produce fullerenes in bulk quantities [11]. The initial fascinating appeal, coming from their beautiful symmetry, shifted later to real chemistry [12]. On the other hand, orientational phenomena which have important role in the properties of fullerenes go back to the high symmetry of these carbon nanostructures [13]. It has been revealed that all fullerene faces are pentagons or hexagons but not all of these polygons are regular.

In the present paper, a problem in mathematical chemistry related to the symmetry of molecules has been considered. Based on the structure of the group, a useful programming language, namely GAP [14], is applied and the character Tables of two fullerenes (C_{24} and C_{28}) is computed. The GAP package is used to find many properties of the groups. We determine the order of these fullerenes cage, conjugacy classes and character table of them.

Theoretical method and result

First of all, we considered the point groups of fullerenes in the case of rigid state (Figures 1 and 3) where the structure was optimized using PM3 method of the chemistry package Hyperchem [15]. Then the point group of C_{24} and C_{28} molecules were determined O_h and T_d, which denoted by G and K, respectively.

The group theory of these fullerenes can be computed using the GAP function Group for O_h point group. Our computations were carried out using the "Groups, Algorithms and Programming" (GAP) system [14]. GAP is a free and extensible software package for computation in discrete abstract algebra, in which you can write your own programs in the GAP language and use them in the same way the programs form part of the system in use. More information on the motivation and development of GAP to date can be found on the GAP web page (http://www.gapsystem.org/).

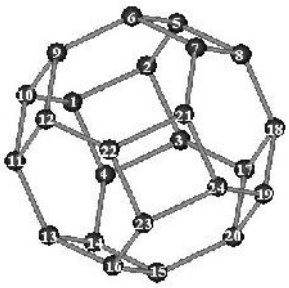

Figure 1. The structure of fullerene C_{24} with O_h symmetry

Determination of conjugacy classes and character table of C_{24}

First of all, we consider the point group O_h of C_{24} fullerene and its tetragonal and hexagonal faces. From the Figure 1, we have three rotations of α_1, α_2 and α_3 ,corresponding to three C_4 axes (Figure 2(a)), three reflectionsβ_1, β_2 and β_3, corresponding to three $\pm$ plans (Figure 2(b)), and four rotations γ_1, γ_2, γ_3 and γ_4 corresponding to four C_3 axes (Figure 2(c)). The permutations (α_1, α_2, α_3, β_1, β_2, β_3, γ_1, γ_2, γ_3 and γ_4) generate the group G.

α_1=(1,2,3,4)(5,17,14,10)(6,18,15,11)(8,20,13,9)(7,19,16,12)(21,24,23,22);

α_2=(5,6,7,8)(2,9,21,18)(1,12,24,17)(3,10,22,19)(4,11,23,20)(13,16,15,14);

α_3=(9,10,11,12)(1,13,22,6)(2,14,23,7)(4,16,21,5)(3,15,24,8)(17,20,19,18);

β_1=(1,2)(3,4)(5,10)(6,9)(7,12)(8,11)(13,18)(14,17)(15,20)(16,19)(21,22)(23,24);

β_2=(5,6)(7,8)(1,10)(2,9)(3,12)(4,11)(18,21)(19,24)(17,22)(20,23)(13,14)(15,16);

β_3=(9,10)(11,12)(1,6)(2,5)(3,8)(4,7)(13,22)(14,21)(15,24)(16,23)(17,18)(19,20);

γ_1=(1,5,9)(2,6,10)(3,7,11)(4,8,12)(17,21,13)(18,22,14)(19,23,15)(20,24,16);

γ_2=(1,14,11)(4,13,10)(2,15,12)(3,16,9)(6,17,23)(20,22,5)(7,18,24)(8,19,21);

γ_3=(6,21,12)(7,22,9)(8,23,10)(5,24,11)(1,18,16)(19,13,2)(3,20,14)(4,17,15);

γ_4=(2,8,17)(3,5,18)(1,7,20)(6,19,4)(9,24,14)(10,21,15)(11,22,16)(12,23,13);

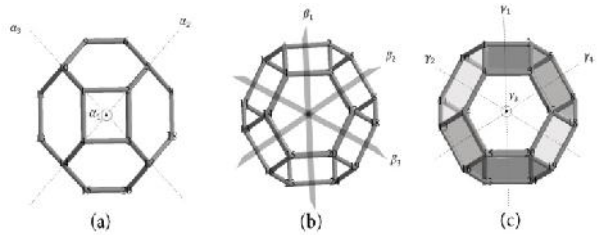

Figure 2. The symmetry elements of the O_h point group of C_{24} fullerene

By using the GAP functions ConjugacyClasses() and Irr(), the conjugacy classes and the character table could be computed, respectively [16,17]. The representative for conjugacy classes of G is given in Table 1.

Also the character table of G can be easily computed using GAP function Irr(G). From conjugacy classes of the groups G, we

are able to compute the irreducible character table of them. Utilizing the conjugacy classes of the group G in the last section, the whole irreducible character table of G can be computed directly or by using GAP. The values of the irreducible characters χ_i ($1 \le i \le 10$) are illustrated at Table 2.

Now, by comparing table 2 with O_h character table which affirm the computing is correct.

Table 1. Representative of conjugacy classes of G

No.	Representative	Size	Name	Symmetry
1	( )	1	**1a**	1 (E)*
2	(2,4)(5,14)(6,13)(7,16)(8,15)(9,11)(18,20)(21,23)	3	**2a**	$_1\sim_1^{-1}$
3	(1,2)(3,4)(5,10)(6,9)(7,12)(8,11)(13,18)(14,17)(15,20)(16,19)(21,22)(23,24)	6	**2b**	$_1$
4	(1,2,3,4)(5,17,14,10)(6,18,15,11)(7,19,16,12)(8,20,13,9)(21,24,23,22)	6	**4a**	$\sim_1$
5	(1,3)(2,4)(5,14)(6,15)(7,16)(8,13)(9,20)(10,17)(11,18)(12,19)(21,23)(22,24)	3	**2c**	$\sim_1^2$
6	(1,5,9)(2,6,10)(3,7,11)(4,8,12)(13,17,21)(14,18,22)(15,19,23)(16,20,24)	8	**3a**	$¥_1$
7	(1,5,18,24,16,11)(2,8,19,23,13,10)(3,7,20,22,14,9)(4,6,17,21,15,12)	8	**6a**	$_1\sim_1^{-1}¥_1$
8	(1,8)(2,5)(3,6)(4,7)(9,17)(10,18)(11,19)(12,20)(13,24)(14,21)(15,22)(16,23)	6	**2d**	$\sim_2^{-1}¥_4^{-1}$
9	(1,8,22,15)(2,7,23,14)(3,6,24,13)(4,5,21,16)(9,19,11,17)(10,18,12,20)	6	**4b**	$_1\sim_1^{-1}\sim_2^{-1}¥_4^{-1}$
10	(1,24)(2,23)(3,22)(4,21)(5,16)(6,15)(7,14)(8,13)(9,20)(10,19)(11,18)(12,17)	1	**2e**	$_1\sim_1^{-1}\sim_2^2$

* *R*otation by 360° is called the Identity operation and is denoted by *E* or *I*

It suffices to note that 1a, 3a, 4a, 2d, 2c, 2e, 2b, 6a, 2a and 4b are E, $8C_3$, $6C_4$, $6C_2$, $3C_2$, i, $6S_4$, $8S_6$, $3\sigma_h$ and $6\sigma_d$, respectively.

Table 2. Character table of the group *G*

O_h	**1a**	**2a**	**2b**	**4a**	**2c**	**3a**	**6a**	**2d**	**4b**	**2e**
i_1	1	1	1	1	1	1	1	1	1	1
i_2	1	-1	-1	1	1	1	-1	1	-1	-1
i_3	1	-1	1	-1	1	1	-1	-1	1	-1
i_4	1	1	-1	-1	1	1	1	-1	-1	1
i_5	2	-2	0	0	2	-1	1	0	0	-2
i_6	2	2	0	0	2	-1	-1	0	0	2
i_7	3	-1	-1	1	-1	0	0	-1	1	3
i_8	3	-1	1	-1	-1	0	0	1	-1	3
i_9	3	1	-1	-1	-1	0	0	1	1	-3
i_{10}	3	1	1	1	-1	0	0	-1	-1	-3

Also, numbers of class members are compatible with their size in Table 1. In addition, the irreducible representations, i_1 to i_{10}, are corresponding to A_{1g}, A_{1u}, A_{2u}, A_{2g}, E_u, E_g, T_{2g}, T_{1g}, T_{1u} and T_{2u}, respectively. So, we can use this method for other fullerenes with unclear symmetry and point group.

Then, we consider the C-C stretches in fullerene and determine the number of unchanged bonds under the symmetry operations of the O_h point group and determine C-C stretching in fullerene using reducible representations and reduction formula ($\Gamma_{\pm}$ is unchanged bonds):

Oh	1(1a)	3(2a)	6(2b)	6(4a)	3(2c)

	8(3a)	8(6a)	6(2b)	6(4b)	1(2e)
$\Gamma_{\pm}$	36	4	0	2	0
	0	0	0	6	0

Using reducible representations and the reduction formula, we obtain following modes:

$$\Gamma_{\pm} = 2i_1 + i_3 + i_5 + 2i_6 + 3i_7 + i_8 + 3i_9 + 2i_{10}$$

Therefore, it means that we have determined vibrational modes:

$$\Gamma_{\pm} = 2A_{1g} + A_{2u} + E_u + 2E_g + 3T_{2g} + T_{1g} + 3T_{1u} + 2T_{2u}$$

Notice, T_{1u} mode is IR active and A_{1g}, E_g, and T_{2g} modes are Raman active.

First of all, we consider the point group, T_d, of C_{28} fullerene (This symmetry is the highest symmetry than the other). Figure 4 illustrates that there are four elements α_1, α_2, α_3 and α_4, corresponding to four rotations C_3 axes (Figure 4(a)), the element $\beta_1$corresponding to the rotation C_2 axes (Figure 4(b)), and six elements γ_1, γ_2, γ_3, γ_4, γ_5 and γ_6 corresponding to sixreflections ± plans (Figure 4(c)). The permutations (α_1, α_2, α_3, α_4, β_1, γ_1, γ_2, γ_3, γ_4, γ_5 and γ_6) generate the group K.

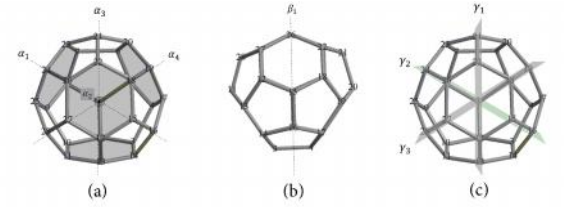

Figure 4. The symmetry elements of the T_d point group of C_{28} fullerene

Then, we have:

α_1=(8,23,25)(1,21,28)(7,24,9)(6,26,10)(5,22,11)(20,27,2)(14,15,17)(4,13,18)(19,3,12);

α_2=(22,15,27)(21,16,28)(23,17,11)(24,19,13)(26,18,12)(6,3,9)(7,4,10)(25,20,14)(8,5,2);

α_3=(2,14,11)(1,16,28)(3,13,10)(4,12,9)(5,15,25)(8,17,27)(20,23,22)(19,7,26)(6,24,18);

α_4=(5,20,17)(1,21,16)(8,22,14)(6,19,4)(7,18,3)(11,27,25)(9,13,26)(24,10,12)(23,15,2);

β_1=(1,21)(2,22)(3,26)(4,24)(5,23)(6,7)(8,20)(9,19)(10,18)(11,15)(12,13)(14,27)(16,28)(17,25);

γ_1=(20,23)(6,7)(24,19)(26,18)(5,8)(25,17)(4,9)(27,15)(28,16)(10,3)(14,11);

γ_2=(23,25)(21,28)(22,27)(20,11)(18,12)(19,13)(17,14)(7,9)(4,3)(2,5)(6,10);

γ_3=(20,17)(15,22)(21,16)(23,14)(26,12)(24,13)(25,11)(6,4)(7,3)(8,2)(9,10);

γ_4=(1,16)(2,14)(25,27)(10,13)(9,12)(8,15)(5,17)(6,19)(7,18)(22,23)(24,26);

γ_5=(1,28)(15,17)(4,12)(3,13)(5,27)(2,11)(8,25)(7,24)(6,26)(22,20)(19,18);

γ_6=(1,21)(2,22)(5,20)(3,18)(8,23)(4,19)(14,15)(13,12)(9,24)(10,26)(11,27);

Table 3. Representative of conjugacy classes of K

No.	Representative	Size	Name	symmetry
1	()	1	1a	E
2	(3,10)(4,9)(5,8)(6,7)(11,14)(15,27)(16,28)(17,25)(18,26)(19,24) (20,23)	6	2a	¥$_1^{-1}$
3	(2,5,8)(3,6,9)(4,7,10)(11,17,23)(12,18,26)(13,19,24)(14,20,25)(15,22,27) (16,21,28)	8	3a	~$_2^{-1}$
4	(1,16,28,21)(2,15,25,20)(3,12,24, 6)(4,13,26,7)(5,14,27,23)(8,17,11,22) (9,19,10,18)	6	4a	$_1^{-1}$~$_2^{-1}$¥$_1^{-1}$
5	(1,16)(2,17)(3, 4)(5,14)(6,13)(7,12)(8,15)(9,18)(10,19)(11,20) (21,28) (22,25)(23,27)(24,26)	3	2b	~$_2^{-1}$ $_1^{-1}$~$_2^{-2}$

The permutations (α_1, α_2, α_3, α_4, β_1, γ_1, γ_2, γ_3, γ_4, γ_5 and γ_6) generate the group K and a simple GAP program shows that K is a group of order 24 with 5 conjugacy classes. The conjugacy classes of K can be computed. The representative for conjugacy classes of K is given in Table 3. Using the permutations (α_1, β_1 and γ_1), the same conclusions are obtained. Also, the character table of K can be easily computed using GAP function Irr(K). From conjugacy classes of the groups K, we able to compute the irreducible character table of them. The values of the irreducible character $\mathrm{i}_i\,(1 \le i \le 5)$ for T_d symmetry is shown in Table 4.

Table 4. Character table of the group *K*

T_d	1a	2a	3a	4a	2b
i_1	1	1	1	1	1
i_2	1	-1	1	-1	1
i_3	2	0	-1	0	2
i_4	3	-1	0	1	-1
i_5	3	1	0	-1	-1

Now, we see table 4 is Td character table. It suffices to note that 1a, 3a, 2a and 4a are E, $8C_3$, $3C_2$, $6S_4$ and $6\sigma_d$, respectively. Also, their sizes are correct. In addition, the irreducible representations, i_1 to i_5, are corresponding to A_1, A_2, E, T_1 and T_2, respectively. Then, we consider the bond stretches in fullerene and determine the number of unchanged bonds under the symmetry operations of the T_d point group and determine $\Gamma_{\pm}$ in this fullerene using reducible representations and reduction formula:

T_d | 1(1a) 8(3a) 3(2b) 6(4a) 6(2a)

$\Gamma_{\pm}$ | 42 0 2 0 4

Using reducible representations and the reduction formula, we obtain following modes:

$$\Gamma_{\pm} = 3\mathrm{i}_1 + \mathrm{i}_2 + 4\mathrm{i}_3 + 4\mathrm{i}_4 + 6\mathrm{i}_5$$

Therefore, it means that we have determined vibrational modes:

$$\Gamma_{\pm} = 3A_1 + A_2 + 4E + 4T_1 + 6T_2$$

Notice, T_2 mode is IR active and A_1, E and T_2 modes are Raman active. We guess that the infrared spectrum peak of $C_{28}(T_d)$ cage is related to T_2 mode.

Conclusion

The method described in this paper appears to be more efficient in dealing with the construction of the character table of symmetry group of the molecule. The structure of the group of full symmetries of a non-rigid molecule with different symmetries is determined by examining various concepts and construction in group theory. First, all the permutations and inversions which don't change the whole framework of the molecule should be examined. Then, using the GAP package, the character table is computed. The symmetry groups of two fullerenes C_{24} and C_{28} with their point groups are studied and the conjugacy classes and the irreducible character tables of them are calculated. Also, this method is usually very useful for calculating symmetries of the molecule, when the numbers of vertices are at most 30 such as the large fullerenes. It is hoped that the present study would help to interpret Raman and IR spectra of fullerenes and fullerene derivatives and another molecules in future.

Acknowledgments

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References

[1] Y.G. Smeyers, *Adv. Quantum Chem.*, **1992**, *24*, 1-77.

[2] K. Balasubramanian, *J. Phys. Chem.*, **2004**, *108*, 5527-5536.

[3] A.R. Ashrafi, M. Hamadanian, *Croat. Chem. Acta*, **2003**, *76*, 299-303.

[4] M. Hamadanian, A.R. Ashrafi, *Croat. Chem. Acta*, **2003**, *76*, 305-312.

[5] T. Karimi, M. Eslami Moghadam, M. Farrokhi D.G., M. Aghaei, *J. Argent. Chem. Soc.*, **2011**, *98*, 60-70.

[6] R.K. Gupta, *Physics of Particles, Nuclei and Materials, Recent Trends*, Edition: **2002**, Chapter: 10, Publisher: Narosa Publishing House, pp.171-192.

[7] S.C. O'Brien, J.R. Heath, R.F. Curl, R.E. Smalley, *J. Chem. Phys.* **1988**, *88*, 220-230.

[8] T. Guo, M.D. Diener, Y. Chai, M.J. Alford, R.E. Haufler, S.M. Mcclure, T. Ohno, J.H. Weaver, G.E. Scuseria and R.E. Smalley, *Science*, **1992**, *257*, 1661-1664.

[9] J. Sun, S. Caltapanides, H.F. Grutzmacher, *J. Phys. Chem. A*, **1998**, *102(14)* 2408-2414.

[10] H. Prinzbach, A. Weiler, P. Landenberger, F. Wahl, J. Wörth, L.T. Scott, M. Gelmont, D. Olevano and B.V.

Issendorff: Nature (London) **2000**, *407*, 60–63.

[11] H. Liu, H. Weng, J. Dong, *J. Mol. Struc.(Theochem),* **2004**, *671*, 93–95.

[12] A. Hirsh and M. Brettreich, (Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim), **2005**, 409-411.

[13] G.R. Vakili-Nezhaad and A.R. Ashrafi , *J. Phys.: Conf. Ser.*, **2006**, 29, 14–17.

[14] The GAP Group, GAP-Groups, Algorithms, and Programming, Version 4.4.12 (**2008**) (http://www.gap-system.org/).

[15] Hyperchem, Version 8.0.7 (**2009**) (http://www.hyper.com/).

[16] M. Eslami Moghadam, T. Karimi, M. Farrokhi D.G., *Int. J. Phys. Sci.*, **2011**, *7(1)* 73-80.

[17] M. Eslami Moghadam, T. Karimi, M. Farrokhi D.G., *Int. J. Phys. Sci.*, **2011**, *1(6)* 57-63.