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The Number of Permutational Isomers of CL-20 Molecule

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Abstract

CL-20 or (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) belongs to the class of high energy nitramine explosives. In this paper, a method of Fujita is applied to compute the number of isomers of this molecule.

1. Introduction

A rigid molecule is defined as being such that the barriers between its versions are insuperable and there are no observable tunneling splittings. For non-rigid molecules, there are one or more contortional large amplitude vibrations such as inversion or internal rotation that give rise to tunneling splittings. Following Y. G. Smeyers [1,2] the non-rigid molecule group (NRG) will be strictly defined as the complete set of the molecular conversion operations, which commute with a given nuclear Hamiltonian operator, limited to large amplitude motions. In addition, these molecular conversation operations will be expressed in terms of physical operations, such as rotations, internal rotations, inversions, similarly as in the Altmann's theory, rather than in terms of permutations and permutations-inversions [3].

The molecular symmetry group is first defined by Longuet-Higgins [4]. Although there have been earlier works that suggested the need for such a framework. In some research papers [5-8], the authors proposed efficient computational techniques for computing molecular symmetry group of moleculaes.

In chemistry, isomers are compounds with the same molecular formula but different structural formulas. There are two main forms of isomerism: structural isomerism and stereoisomerism. In this paper we focus on the problem of counting structural isomerism of CL-20 or (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaiso-wurtzitane) molecule, Figure 1.

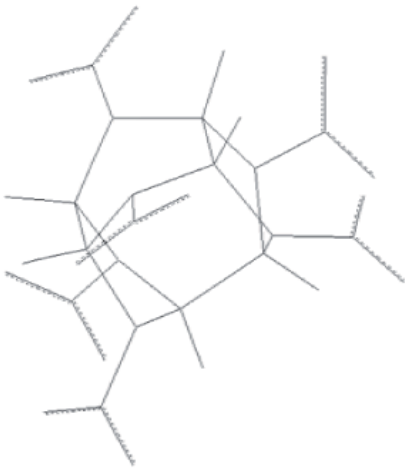

Figure 1. The Molecular Structure of CL-20 Molecule.

For computing the number of isomers of a given molecule, we need to an efficient method for computing symmetry of molecule under consideration. Fripertinger [9] computed the symmetry of some fullerenes and then applied SYMMETRICA [10] to calculate the number of $C_{60}H_kCl_{60-k}$ molecules and Balasubramanian [11] computed the number of $C_{60}H_{36}$ isomers.

Throughout this paper, our notation is standard and taken mainly from [12,13]. We encourage to the readers to consult papers [12-20] for background material as well as basic computational techniques.

2. Main Results and Discussion

In mathematics, "Computational Group Theory" is the study of groups by means of computers. It is concerned with designing and analyzing algorithms and data structures. The most famous starting point for enumeration under group action is an important paper of Polya in which he not only describes cycle index techniques for determining the numbers of orbits under finite group actions but he demonstrates how to apply these methods for the chemical problem of isomer enumeration as well. The aim of this section is to enumerate the number of isomers of CL-20. We first compute the symmetry group of this molecule. Here, symmetry means automorphism group symmetry. To do this, the molecule is drawn by HyperChem [21] and then we compute its adjacency matrix by TopoCluj [22].

Let G be a permutation group, a subgroup of a given symmetric group S_X on X. The orbit of x will be denoted by Gx and defines as the set of all g(x), $g \in G$. The set of all G-orbits will be denoted by $G\backslash\backslash X := \{ Gx \mid x \in X\}$. Suppose g is a permutation of n symbols with exactly λ_1 orbits of size 1, λ_2 orbits of size 2, …, and λ_n orbits of size n. Then the cycle type of g is defined as $1^{\lambda_1}2^{\lambda_2}...n^{\lambda_n}$.

Let G be a permutation group. The cycle index of G acting on X is the polynomial Z(G, X) over Q in terms of indeterminates x_1, x_2, …, x_t, t = |X|, defined by $Z(G, X) = \frac{1}{|G|}\sum_{p\in G}\prod_{i=1}^{t} x_i^{c_i(p)}$, in which $(c_1(p), \cdots, c_t(p))$ is the cycle type of the permutation $p \in G$. The generalized character cycle index is defined as

$$P_G^{\chi}(x_1, x_2, ..., x_t) = \frac{1}{|G|}\sum_{p\in G}\prod_{i=1}^{t}\chi(p)x_i^{c_i(p)}$$

where $\chi(g)$ is the linear character of the irreducible representation of *G*. In this paper we use two special cases: One is the anti-symmetric representation, that is

$$\chi(g) = \begin{cases} 1 & \text{if } g \text{ is a proper rotation}, \\ -1 & \text{if } g \text{ is an improper rotation}, \end{cases}$$

and the other when χ is 1 for all *g*. Since, all elements of a conjugacy class of a permutation group have the same cycle type, so the cycle index and the generalized character cycle index can be rephrased in the following way:

$$Z(G, x_1, \ldots, x_t) = \frac{1}{|G|}\sum_{C\in Conj(G)} |C| \prod_{i=1}^{t} x_i^{c_i(g_C)},$$

$$P_G^{\chi}(x_1, \ldots, x_t) = \frac{1}{|G|}\sum_{C\in Conj(G)} |C| \prod_{i=1}^{t} \chi(g_c) x_i^{c_i(g_C)}.$$

In order to apply the Polya-Redfield theorem, we first calculate permutations generating the symmetry group of CL-20. These are:

a:= (1,4) (2,5) (3,6) (7,9) (8,10) (11,12) (13,15) (14,16)(17,18) (19,23,20,24) (21,25,22,26) (27,29,28,30) (31,32)(33,35) (34,36);

b:= (1,4) (2,5) (3,6) (7,9) (8,10) (11,12) (13,15) (14,16) (17,18) (19,23) (20,24) (21,25) (22,26) (27,29) (28,30) (31,32) (33,35) (34,36);

c:= (1,6) (2,5) (3,4) (7,10) (8,9) (14,15) (13,16) (19,25,20,26) (21,23,22,24) (27,28) (29,30) (31,32) (33,36) (34,35);

d:= (1,3) (4,6) (7,8) (9,10) (11,12) (13,14) (15,16) (17,18) (19,21,20,22) (23,25,24,26) (27,30,28,29) (33,34)(35,36);

e:= (21,22);

Define G = <a,b,c,d,e>. Then G is a group of order 256 with a center of order 4 and $\frac{G}{G'} \cong Z_2 \times Z_2 \times Z_2 \times Z_2$. From these group structures and a simple GAP program [18], the number of isomers of CL-20 are calculated in Table 1.

Table 1. The Number of Permutational Isomers of CL-20.

[k,36-k]	Number of Isomers
0,36	1
1,35	10
2,34	126
3,33	1098
4,32	7608
5,31	41506
6,30	186284
7,29	700870
8,28	2257287
9,27	6305720
10,26	15459528
11,25	33543976
12,24	64878097
13,23	112448242
14,22	175424244
15,21	247116838
16,20	315124911
17,19	364364236
18,18	382396468

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References

1. Y. G. Smeyers, M. Villa, E. Ortiz, The non-rigid group for wagging and torsion modes in methvlamine, *J. Math. Chem.* **18** (1995) 209-216.
2. Y. G. Smeyers, Introduction to group theory for non-rigid molecules, Adv. Quantum Chem. **24** (1991) 1-77.
3. P. R. Bunker, *Molecular Symmetry and Spectroscopy*, Academic Press, New York, 1979.
4. H. C. Longuet-Higgins, The symmetry groups of non-rigid molecules, *Mol. Phys*. **6** (1963) 445-460.
5. A. R. Ashrafi, On non-rigid group theory for some molecules, *MATCH Commun. Math. Comput. Chem.* **53** (2005) 161-174.
6. M. Dabirian, A. Iranmanesh, The full non-rigid group theory for trimethylamine-BH_3 complex, *MATCH Commun. Math. Comput. Chem.* **54** (2005) 75-88.
7. A. R. Ashrafi, On symmetry properties of molecules, *Chem. Phys. Lett.* **406** (2005) 75-80.
8. M. R. Darafsheh, Y. Farjami, A. R. Ashrafi, Symmetries of weighted complete graphs of tetranitrocubane and octanitrocubane, *MATCH Commun. Math. Comput. Chem.* **54** (2005) 331-340.
9. H. Fripertinger, The cycle index of the symmetry group of the fullerene C_{60}, *MATCH Commun. Math. Comput. Chem.* **33** (1996) 121-138.
10. SYMMETRICA, A program system devoted to representation theory, invariant theory and combinatorics of finite symmetric groups and related classes of groups, Copyright by "Lehrstuhl II für Mathematik, Universität Bayreuth, 95440 Bayreuth". Distributed via anonymous ftp 132.180.16.20 in dist/SYM.tar.Z.
11. K. Balasubramanian, Nuclear spin statistics of extended aromatic $C_{48}N_{12}$ azafullerene, *Chem. Phys. Lett.* **391** (2004) 69-74.
12. A. R. Ashrafi, M. Ghorbani, A note on markaracter tables of finite groups, *MATCH Commun. Math. Comput. Chem.* **59** (2008) 595-603.
13. A. R. Ashrafi, M. Ghorbani, Computer application of GAP to the evaluation of numbers of permutational isomers of hetero fullerenes, *MATCH Commun. Math. Comput. Chem.* **60** (2008) 359-367.

14. M. Deza, M. D. Sikirić, P. W. Fowler, The symmetries of cubic polyhedral graphs with face size no larger than 6, *MATCH Commun. Math. Comput. Chem.* **61** (2009) 589-602.
15. B. Taeri, M. Arezooman, The full non-rigid group theory for TBA (tert-butyl alcohol), *J. Iran. Chem. Soc.* **5** (2008) 514-518.
16. M. Arezoomand, B. Taeri, Full non-rigid group of di-mu-oxo-bis (tetraamine manganese(II)) as a wreath product, *MATCH Commun. Math. Comput. Chem.* **62** (2009) 275-284.
17. S. Fujita, Itemized enumeration of quadruplets of rs-stereoisomers under the action of RS-stereoisomeric groups, *MATCH Commun. Math. Comput. Chem.* **61** (2009) 71-115.
18. W. Hässelbarth, A. Kerber, Chirality and permutational isomers, *MATCH Commun. Math. Comput. Chem.* **61** (2009) 149-216.
19. S. Fujita, Systematic comparison between three-dimensional structures and graphs (part 1). The fate of asymmetry and pseudoasymmetry in the enumeration of monosubstituted alkanes, *MATCH Commun. Math. Comput. Chem.* **62** (2009) 23-64.
20. S. Fujita, Systematic comparison between three-dimensional structures and graphs (part 2). The fate of asymmetry and pseudoasymmetry in the enumeration of alkanes, *MATCH Commun. Math. Comput. Chem.* **62** (2009) 65-104.
21. Hyper Chem package Release 7.5 for Windows, Hypercube Inc., 1115 NW 4th Street, Gainesville, Florida 32601,USA, 2002.
22. M. V. Diudea, O. Ursu, C. L. Nagy, TOPOCLUJ, Babes-Bolyai University, Cluj, 2002.