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Automorphism Group and Topological Indices of the Chemical Graph of Fullerenes

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Abstract

In an earlier paper, the authors of this paper designed a MATLAB program for computing symmetry of molecules. They applied this program to calculate the symmetry of the fullerene C_{80}.

In this paper, using a well-known result on graphs, we write another MATLAB program for computing the automorphism group of some fullerene graphs, which has better running time. The PI, Wiener and Schultz indices of these chemical graphs are also computed.

INTRODUCTION

In this section we describe some notations which will be kept throughout. The icosahedral C_{60} molecule discovered by Kroto et al. in 1985 [1] was the first known example of a fullerene: a molecular cage of carbon consisting of fused hexagon and pentagon rings. The interest generated by this discovery led to the identification of many other fullerenes and related structures [2], and in particular to the observation of carbon nanotubes. Fullerenes are a new allotrope of carbon characterized by a closed-cage structure consisting of an even number of three-coordinate carbon atoms devoid of hydrogen atoms. This class was originally limited to closed-cage structures with 12 isolated five-membered rings, the rest being six-membered rings. However, the term has been broadened to include any closed-cage structure having 20 or more carbon atoms consisting entirely of 3 coordinate carbon atoms [3]. The motivation for the study of fullerenes is outlined in the nice book of Korto, Fichier and Cox [4], and the reader is encouraged to consult this book for background material.

Fullerenes with a wide range of numbers of carbon atoms have been produced in experiment. Isomers with 60, 70, 76, 78 and 84 atoms have been produced in sufficient quantity to be characterized by NMR spectroscopy.

The adjacency matrix or Hamiltonian operator $A = [A_{ij}]$ of a graph G with n vertices is the square $n \times n$ symmetric matrix which contains information about the internal connectivity of vertices in the graph. It is defined as

Figure 1

$$A_{ij} = \begin{cases} 1 & \text{if vertices } i \text{ and } j \text{ are connected by an edge} \\ 0 & \text{otherwise} \end{cases}$$

One can see easily the fact that all unitary matrices commuting with the adjacency matrix A of a molecular graph form a group H with this property that:

Figure 2

$$T^{-1}AT = A \quad ; \quad \forall T \in H \tag{1}$$

The group H is called the Hamiltonian group of the graph under consideration and its elements are defined as a generalized symmetry operator. In a real vector space, these matrices are orthogonal. It is well known that the symmetry operators in the point group of a molecule always commute with its Hamiltonian operator [5]. So the group H of molecular graph must contain the point group H_p of the graph, for details see [6]. It is well-known fact that the set of all permutation matrices satisfied in equation (1) constitute the full automorphism group of the molecular graph under consideration. Here a permutation matrix is a matrix that has exactly one 1 in each row or column and 0s elsewhere. Permutation matrices are the matrix representation of permutations.

A topological index is a real number related to a molecular graph. It must be a structural invariant, i.e., it does not

depend on the labelling or the pictorial representation of a graph. There are several topological indices have been defined and many of them have found applications as means to model chemical, pharmaceutical and other properties of molecules. Here, we consider three of topological indices containing Wiener, Padmakar-Ivan (PI) and Schultz index. These topological indices define as follows:

The Wiener index W(G) of a molecular graph G is defined as the sum of the distances between all pairs of vertices. In other words,

Figure 3

$$W(G) = \frac{1}{2}\left(\sum_{i=1}^{n} P_i\right),$$

where P_i is length of the path that contains the least number of edges between vertex i and vertex j in graph G and n is the maximum possible number of i and j, see [7,8,9] for details.

The Padmakar–Ivan (PI) index of a graph G is defined as $PI(G) = \sum_{e \in E}[n_{eu}(e|G) + n_{ev}(e|G)]$, where $n_{eu}(e|G)$ is the number of edges of G lying closer to u than to v, $n_{ev}(e|G)$ is the number of edges of G lying closer to v than to u and summation goes over all edges of G, [10,11,12,13,14].

The Schultz index of a graph G is denoted by MTI(G). It is defined as

Figure 4

$$MTI(G) = \sum_{i=1}^{n}\sum_{j=1}^{n} v_i(A_{ij} + D_{ij})$$

where v_i is the degree of vertex i in G, A_{ij} is equal to unity if vertices i and j are adjacent and zero otherwise and D_{ij} is the length of a shortest path between vertices i and j, [15,16].

The goal of this article is to obtain some computer programs for calculating the Wiener, PI and Schultz indices of molecular graphs. We apply this program on some big fullerenes. We also apply our earlier MATLAB Program [17,18] for computing the automorphism group of fullerenes $C_{20}(1)$, $C_{20}(2)$, C_{60}, C_{70}, C_{80}, C_{140} and C_{150}. Throughout this paper, only finite graphs are investigated. Our notation is standard and taken mainly from Refs. [19,20]. Computations were carried out with the aid of MATLAB [21], and, GAP [22]. We encourage reader to consult [23,24] for applications of GAP in solving problems of chemistry and [25,26,27,28,29] for background material about theoretical aspects of symmetry property of molecules.

COMPUTATIONAL DETAILS

Permutation group theory has been widely applied to various chemical problems related to the symmetry property of a molecule. Symmetry operations on a graph are called also graph automorphisms. They affect only the labels of vertices by permuting them so that the adjacency matrix of the graph remains unchanged. The graph symmetry is completely determined by all the automorphisms it has, i.e. by specifying all the permutations which leave the adjacency matrix intact.

There are potential methods for computing automorphism group of a graph. We use these techniques to solve our problem. In order to deduce the symmetry of a molecule, we have to compute first the n × n adjacency matrix A of the chemical graph under consideration. Then we must solve the matrix equation $P^t A P = P$, in the set of all permutation matrices of size n.

The first author in [17] proved a result that is useful for computing symmetry of molecules. Using this result, Lemma 1 and its Corollary, we present a MATLAB program [18] for computing a solution matrix for the automorphism group of chemical graphs. We believe that MATLAB is the best software for writing such a program, because it uses variables that are defined to be matrices. Since the image of any vertex v of a graph under one of its automorphisms has the same degree as v, we can improve our last program in [18] to find a better running time. In the end of this section we present our new MATLAB program, as follows:

## PROGRAM: A MATLAB PROGRAM FOR COMPUTING THE SYMMETRIES OF MOLECULES

SYMMETRY AND TOPOLOGICAL INDICES OF FULLERENES

The aim of this section is to calculate the automorphism group of chemical graph of the fullerene $C_{20}(1)$, $C_{20}(2)$, C_{60}, C_{70}, C_{80}, C_{140} and C_{150}. To do this, from figure 1, we calculate the adjacency matrices of these fullerene graphs and then apply our MATLAB program for computing a solution matrix for any of these fullerenes. In the final step, we

consider the following simple GAP program for computing the automorphism group of these fullerenes.

Figure 5

Figure 1: Schlegel Diagrams of some Fullerenes

(a) $C_{20}(1)$ (b) $C_{20}(2)$ (c) C_{60} (d) C_{70} (e) C_{140} (f) C_{150}
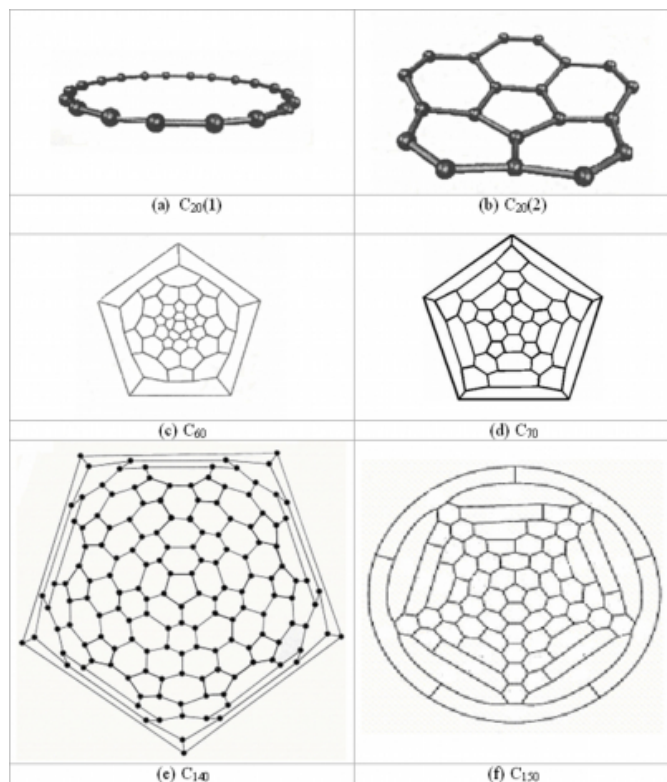
In this program, X denotes the solution matrix computed bt our MATLAB programs. We encourage the reader to consult Refs. [23,24] for more details about GAP and its programming language. In what follows, we calculate a generating set for any of automorphism groups of the fullerene graphs under consideration.

GENERATORS OF THE AUTOMORPHISM GROUPS OF FULLERENES

C(1), C(2), C, C, C, C AND C

$C_{20}(1)^1 =$
(2,20)(3,19)(4,18)(5,17)(6,16)(7,15)(8,14)(9,13)(10,12),

$C_{20}(1)^2 =$
(1,2)(3,20)(4,19)(5,18)(6,17)(7,16)(8,15)(9,14)(10,13)(11,12),

$C_{20}(2)^1 =$
(1,2)(3,15)(4,14)(5,13)(6,12)(7,11)(8,10)(16,17)(18,20),

$C_{20}(2)^2 =$
(1,4,7,10,13)(2,5,8,11,14)(3,6,9,12,15)(16,17,18,19,20),

$C_{60}^1 =$
(2,5)(3,4)(6,8)(9,10)(11,18)(12,17)(13,16)(14,15)(19,20)(21,30)(22,29)(23,28)(24,27)(25,26)(31,32)(33,48)(34,47)(35,46)(36,45)(37,44)(38,43)(39,42)(40,41)(50,55)(51,54)(52,53)(56,59)(57,58),

$C_{60}^2 =$
(1,2)(3,5)(6,9)(7,8)(11,20)(12,19)(13,18)(14,17)(15,16)(21,22)(23,30)(24,29)(25,28)(26,27)(31,36)(32,35)(33,34)(37,48)(38,47)(39,46)(40,45)(41,42)(43,53)(44,52)(49,50)(51,55)(56,58)(59,60),

$C_{60}^3 =$
(1,6,14)(2,12,25)(3,23,26)(4,24,15)(5,13,7)(8,11,40)(9,36,41)(10,39,16)(17,22,52)(18,35,53)(19,37,42)(20,38,27)(21,51,28)(29,34,54)(30,50,43)(31,59,44)(32,58,45)(33,57,46)(47,49,56)(48,60,55),

$C_{70}^1 =$
(3,12)(4,11)(5,10)(6,9)(7,8)(13,14)(15,30)(16,29)(17,28)(18,27)(19,26)(20,25)(21,24)(22,23)(31,32)(33,49)(34,48)(35,47)(36,46)(37,45)(38,44)(39,43)(40,42)(50,51)(52,64)(53,63)(54,62)(55,61)(56,60)(57,59)(65,66)(67,70)(68,69),

$C_{70}^2 =$
(1,4)(2,3)(5,6)(7,19)(8,18)(9,17)(10,16)(11,15)(12,14)(20,21)(22,38)(23,37)(24,36)(25,35)(26,34)(27,33)(28,32)(29,31)(39,40)(41,56)(42,55)(43,54)(44,53)(45,52)(46,51)(47,50)(48,49)(57,58)(59,68)(60,67)(61,66)(62,65)(63,64),

$C_{70}^3 =$
(1,41)(2,58)(3,57)(4,56)(5,39)(6,40)(7,22)(8,23)(9,42)(10,43)(11,60)(12,59)(13,69)(14,68)(15,67)(16,54)(17,55)(18,37)(19,38)(26,44)(27,45)(28,61)(29,62)(30,70)(31,65)(32,66)(33,52)(34,53)(48,63)(49,64),

$C_{80}^1 =$
(2,5)(3,4)(6,8)(9,10)(11,18)(12,17)(13,16)(14,15)(19,20)(21,39)(22,38)(23,37)(24,36)(48,54)(49,53)(50,52)(61,63)(64,75)(65,74)(66,73)(67,72)(68,71)(69,70)(76,79)(77,78)(25,35)(26,34)(27,33)(28,32)(29,31)(42,60)(43,59)(44,58)(45,57)(46,56)(47,55),

$C_{80}^2 =$
(1,2)(3,5)(6,9)(7,8)(11,20)(12,19)(13,18)(14,17)(15,16)(21,2

3)(24,40)(25,39)(26,38)
(50,56)(51,55)(52,54)(61,66)(62,65)(63,64)(67,75)(68,74)(69,73)(70,72)(76,78)(79,80)
(27,37)(28,36)(29,35)(30,34)(31,33)(41,45)(42,44)(46,60)(47,59)(48,58)(49,57),

$C_{80}^{3} =$
(1,11,44,80,72,33)(2,12,43,79,73,32)(3,25,42,78,56,31)(4,24,63,77,55,15)(38,49)
(13,21,66,75,52,17)(14,20,46,61,70,35)(18,27,40,67,58,51)(19,47,60,69,36,29)
(5,23,64,76,54,16)(6,22,65,74,53,8)(7,10,45,62,71,34)(9,26,41,68,57,30) (28,39,48,59,50,37),

$C_{140}^{1} =$
(1,6,7,20,21)(2,5,8,19,22)(3,10,17,24,91)(4,9,18,23,90)(11,16,25,92,87)
(12,48,33,93,86)(13,28,34,94,58)(14,27,35,89,57)(15,26,36,88,56)(29,38,95,59,51)
(30,37,130,55,50)(31,99,129,63,49)(32,98,85,54,47)(39,96,60,52,45)(40,97,83,53,46)
(75,112,106,125,80)(76,114,121,124,140)(77,115,120,123,134)(116,119,122,135,139)
(66,72,109,103,82)(67,113,107,126,81)(73,110,104,133,78)(74,111,105,132,79)
(41,102,84,65,71)(42,101,131,64,70)(43,100,128,62,69)(44,108,127,61,68) (117,118,137,136,138),

$C_{140}^{2} =$
(1,13,74,110,37)(2,12,75,120,99)(3,54,76,121,98)(4,53,116,106,93)(5,52,115,107,92)
(6,51,73,109,36)(57,65,117,105,94)(8,49,113,40,23)(9,69,112,39,22)(10,68,114,108,91)
(11,67,119,100,90)(14,70,111,38,21)(15,71,42,34,20)(16,46,43,33,19)(17,47,44,32,24)
(18,48,45,31,25)(26,27,28,29,30)(55,78,137,102,88)(56,66,118,101,89)(7,50,72,41,35)
(58,64,138,104,95)(59,79,136,103,130)(60,80,135,126,129)(61,140,124,127,85)
(62,139,123,96,86)(63,77,122,97,87)(81,134,125,128,83)(82,133,132,131,84),

$C_{150}^{1} =$
(2,5)(3,4)(6,12)(7,11)(8,10)(13,20)(14,19)(15,18)(16,17)(21,69)(22,72)(23,71)(24,70)
(25,68)(26,67)(27,66)(28,65)(29,64)(30,63)(31,40)(32,41)(33,53)(34,54)(35,42) (36,39)
(46,52)(47,51)(55,147)(56,146)(57,145)(58,138)(59,137)(60,144)(118,120)
(43,45)(61,148)(62,149)(73,150)(74,112)(75,113)(76,143)(77,142)(78,139)(79,111)
(80,109)(81,104)(82,103)(83,102)(84,100)(85,99)(86,105)(87,108)(88,107)(89,106)
(90,98)(91,97)(92,96)(93,94)(95,101)(110,126)(114,125)(115,124)(116,123)(48,50)
(117,122)(119,121)(127,141)(128,131)(129,130)(132,133)(134,140),

$C_{150}^{2} =$
(1,2)(3,5)(6,15)(7,14)(8,13)(9,12)(10,11)(16,20)(17,19)(21,95)(22,92)(23,91)(24,90)
(25,85)(26,84)(27,83)(28,82)(29,81)(30,86)(31,72)(32,71)(33,79)(34,80)(35,70)
(36,69)(37,67)(38,68)(39,66)(40,65)(41,64)(42,63)(43,62)(44,61)(45,73)(46,74)
(47,75)(48,76)(49,60)(50,57)(51,56)(52,55)(53,54)(58,59)(77,137)(78,136)(87,149)
(88,148)(89,150)(113,120)(114,118)(115,117)(122,143)(123,144)(124,145)(125,146)
(126,147)(127,138)(93,111)(94,109)(96,103)(97,104)(98,105)(101,102)(106,108)
(110,119)(112,121)(128,139)(129,142)(130,141)(133,140)(134,135),

$C_{150}^{3} =$
(1,132)(2,133)(3,134)(4,135)(5,140)(6,139)(7,142)(8,141)(9,131)(10,130)(11,129)
(12,128)(13,127)(14,77)(15,78)(16,58)(17,59)(18,136)(19,137)(20,138)(21,145)
(22,146)(23,147)(24,149)(25,148)(26,144)(27,143)(28,113)(29,112)(30,150)(31,114)
(32,110)(33,109)(34,111)(35,108)(36,115)(37,116)(38,107)(39,117)(40,118)(41,119)
(42,106)(43,98)(44,99)(45,105)(46,104)(47,103)(48,102)(49,100)(50,101)(51,96)
(52,97)(53,94)(54,93)(55,91)(56,92)(57,95)(60,84)(61,85)(62,90)(63,89)(64,121)
(65,120)(66,122)(67,123)(68,88)(69,124)(70,87)(71,126)(72,125)(73,86)(74,81) (75,82)(76,83)(79,80).

We now write a MATLAB program for computing Wiener, PI and Schultz indices of these fullerenes.

A MATLAB PROGRAM FOR COMPUTING THE WIENER, PI AND SCHULTZ INDICES

In Table 1, we calculate these topological indices, their running times and the order of symmetry group for the mentioned fullerenes.

Figure 6

Table 1: The Values of Wiener, PI and Schultz Indices of Fullerenes

	Running Time of Wiener Index	Running Time of PI Index	Running Time of Schultz Index	Wiener index	PI index	Schultz index	Order of Symmetry Group
$C_{20}(1)$	0.593	0.594	0.594	1000	360	4080	40
$C_{20}(2)$	0.593	0.579	0.578	615	540	3130	10
C_{60}	1.078	1.079	1.063	8340	7200	50580	120
C_{70}	1.734	1.734	1.703	12375	9930	74880	20
C_{80}	2.563	2.578	2.547	17600	13080	106320	120
C_{140}	13.547	13.625	13.578	71390	41010	429600	60
C_{150}	16.812	16.953	17	84920	47097	510870	20

C(1), C(2), C, C, C, C AND C AND THE ORDER OF THEIR AUTOMORPHISM GROUP SYMMETRY

In the end of this paper we pose the following open questions:

Conjecture 1: If G is a fullerene graph then PI(G) < W(G), where W(G) denotes the Wiener index of G.

Conjecture 2: Suppose $G_1, G_2, ...$ is a sequence of fullerene graphs such that all of them has a given group E as automorphism group and $|V(G_1)|, |V(G_2)|, ...$ is an increasing sequence of natural numbers. Then

Figure 7

$$\text{Lim}_{n \to \infty} \frac{PI(G)}{W(G)} = \frac{1}{2}.$$

We mention here that the figure of fullerenes in Figure 1 taken from the internet. Unfortunately, we don't have its exact address to cite here.

References

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley: "C60: Buckminsterfullerene", Nature, Vol. 318, (1995), pp. 162-163.
2. M. Terrones, W. K. Hsu, J. P. Hare, H. W. Kroto, H. Terrones and D. R. Walton: "Graphitic structures: from planar to spheres, toroids and helices", Phil. Trans. R. Soc. Lond. A, Vol. 354, (1996), pp. 2025-2054.
3. A. L. Goodson, C. L. Gladys, D. E. Worst: "Numbering and Naming of Fullerenes by Chemical Abstracts Service", J. Chem. Inf. Comp. Sci., Vol. 35, (1995), pp. 969-978.
4. H. W. Kroto, J. E. Fischer and D. E. Cox: Eds., The Fullerene, Pergamon Press, New York, 1993.
5. F. A. Cotton: Chemical Applications of Group Theory, Wiley, New York, 1990.
6. J. Liu, "Hidden symmetry in molecular graphs", J. Chem. Soc., Faraday Trans., Vol. 93, (1997), pp. 5-9.
7. H. Wiener: "Structural determination of the paraffin boiling points", J. Am. Chem. Soc., Vol. 69, (1947), pp. 17-20.
8. A. A. Dobrynin, R. Entringer and I. Gutman: "Wiener index of trees: theory and applications", Acta Appl. Math., Vol. 66, (2001), pp. 211-249.
9. A. A. Dobrynin, I. Gutman, S. Klavžar, P. Žigert: "Wiener index of hexagonal systems", Acta Appl. Math., Vol. 72, (2002), pp. 247-294.
10. P. V. Khadikar: "On a Novel Structural Descriptor PI", Nat. Acad. Sci. Lett., Vol. 23, (2000), pp. 113-118.
11. P. V. Khadikar, S. Karmarkar and V. K. Agrawal: "PI Index of Polyacenes and its Use in Developing QSPR", Nat. Acad. Sci. Lett., Vol. 23, (2000), pp. 124-128.
12. P. V. Khadikar, P. P. Kale, N. V. Deshpande, S. Karmarkar and V. K. Agrawal: "Novel PI Indices of Hexagonal Chains", J. Math. Chem., Vol. 29, (2001), pp. 143-150.
13. P. V. Khadikar, S. Karmarkar and V. K. Agrawal: "A Novel PI Index and its Applications to QSPR/QSAR Studies", J. Chem. Inf. Comput. Sci., Vol. 41, (2001), pp. 934-949.
14. P. V. Khadikar, S. Karmarkar and R. G. Varma: "The Estimation of PI Index of Polyacenes", Acta Chim. Slov., Vol. 49, (2002), pp. 755-771.
15. H. P. Schultz: "Topoloical organic chemistry. 1. Graph theory and topological indices of alkanes", J. Chem. Inf. Comput. Sci., Vol. 29, (1989), pp. 227-228.
16. A. A. Dobrynin: "Explicit Relation between the Wiener Index and the Schultz Index of Catacondensed Benzenoid Graphs", Croat. Chem. Acta, Vol. 72, (1999), pp. 869-874.
17. A.R. Ashrafi: "On symmetry properties of molecules", Chem. Phys. Lett., Vol. 406, (2005), pp. 75-80.
18. A.R. Ashrafi and M.R. Ahmadi: "New computer program to calculate the symmetry of molecules", Cent. Eur. J. Chem., Vol. 3, (2005), pp. 647-657.
19. N. Trinajstic: Chemical Graph Theory, CRC Press, Boca Raton, FL. 1992.
20. F. Harary: Graph Theory, Addison-Welsey, Reading, MA, 1969.
21. D.J. Higham and N.J. Higham: MATLAB Guide, Society for Industrial and Applied Mathematics (SIAM), Philadelphia, PA, 2000.
22. M. Schönert, H.U. Besche, Th. Breuer, F. Celler, B. Eick, V. Felsch, A. Hulpke, J. Mnich, W. Nickel, G. Pfeiffer, U. Polis, H. Theißen and A. Niemeyer: GAP, Groups, Algorithms and Programming, Lehrstuhl De für Mathematik, RWTH, Aachen, 1995.
23. A. R. Ashrafi: On Non-Rigid Group Theory For Some Molecules, MATCH Commun. Math. Comput. Chem., Vol. 53, (2005), 161-174.
24. A.R. Ashrafi and M. Hamadanian: "Symmetry Properties of Some Chemical Graphs", Croat. Chem. Acta, Vol. 78, (2005), pp. 159-163.
25. K. Balasubramanian: "Graph-Theoretical Perception of Molecular Symmetry", Chem. Phys. Letters, Vol. 232, (1995), pp. 415-423.
26. K. Balasubramanian: "The Symmetry Groups of Chemical Graphs", Int. J. Quant. Chem., Vol. 21, (1982), pp. 411-418.
27. K. Balasubramanian: "Applications of Combinatorics and Graph Theory to Spectroscopy and Quantum Chemistry", Chem. Rev., Vol. 85, (1985), pp. 599-618.
28. K. Balasubramanian: "Group Theoretical Analysis of Vibrational Modes and Rovibronic Levels of extended aromatic C48N12 Azafullerene", Chem. Phys. Letters, Vol.

391, (2004), pp. 64-68.

29. K. Balasubramanian: "Nuclear Spin Statistics of extended aromatic $C_{48}N_{12}$ Azafullerene", Chem. Phys. Letters, Vol. 391, (2004), pp. 69-74.

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