Enumeration of isomers of substituted fullerene cages $C_{20} - C_{50}$

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We use computerized enumerative combinatorial techniques which employed quadruple precision arithmetic to enumerate the isomers of polysubstituted fullerene cages $C_{20} - C_{50}$.

1. Introduction

Fullerene chemistry has provided a new dimension of aromaticity and a new platform for discussion of mathematical techniques pertinent to large cages. Experimental studies on fullerene cages are on considerable increase in recent years [1–8]. There are myriads of such studies which have culminated in both synthesis and characterization of carbon cages and their derivatives of varied shapes and sizes. Recently, Birkett et al. [8] have synthesized halogen derivatives of the buckyball such as $C_{60}Br_8$ and $C_{60}Br_6$. Mathematical and theoretical studies on such clusters and cages [9–21] are both formidably difficult and challenging due to combinatorial possibilities and a large number of electrons.

Recently, there has become increased interest in smaller fullerene cages. Smalley and co-workers [7] have reported unusually metal-stabilized $C_{28}$ cages. In particular they reported U@$C_{28}$ (uranium inside the $C_{28}$ cage). The $C_{28}$ cluster appears to be the smallest fullerene cage to be found in large abundance, although mathematically the smallest possible fullerene is $C_{20}$. Hydrogen and halogen derivatives of fullerenes have also been reported [5,6,8].

Since chemical reactions of fullerene cages and spectroscopic studies on these cages are becoming increasingly important, structures and possible isomers of these cages need to be established. Alternatively, from the possible isomers of a cage, the structure of the cage could be established. For example, there are at least two $C_{40}$ fullerene cages with different structures which are shown in this study to have different isomer counts. Consequently, isomer counts at different levels of substitution could provide potentially powerful structural discriminators for the carbon cages. In the present investigation we enumerate some structures for carbon cages for $C_n$ ($n = 20–60$) and possible isomers for compounds such as $C_nH_m$, $C_nH_mX_k$ for different values of $m$ and $k$. The isomer counts for some particular values of $m$ and $k$ are also extremely useful in the enumeration of NMR signals and would thus provide valuable information on the number of NMR signals for the various fullerene cages considered here. We employ powerful computerized combinatorial techniques in conjunction with the quadruple precision arithmetic to enumerate the isomers of polysubstituted fullerene cages. We consider feasible $C_{20} - C_{50}$ cages.

2. Method of enumeration and computation

The procedure used to enumerate the isomers of polysubstituted fullerene cages is based on Pólya's theorem [22] and has been described before in details [23–26] in the chemical context. In this method the generating function for the isomers is obtained using the cycle index of the rotational subgroup of the point group of the fullerene cage under consideration. Suppose $G$ is the rotational subgroup, then the cycle index $P_G$ is defined as
The use of Pólya's theorem in the chemical context has been a subject of several studies [19,23–26]. We will therefore not illustrate the procedure with examples since this has been done before. The method has already been implemented on a computer [25,26]. The main difficulty in applying the code developed by the author [25] before to fullerene cages is that integer/real overflows occur due to the large numbers that are computed. This was circumvented as described in a recent paper [15] by a special algorithm to evaluate multinomial numbers and through the use of double or quadruple precision arithmetic to uniformly compute all coefficients in the generating function. We use this version of the code employing real*16 arithmetic and a recursive division algorithm for multinomial numbers described before [15]. It is interesting to note that the isomerization of \( C_{60} \) fullerene has been discussed in the literature [26].

3. Results and discussion

Fig. 1 shows the fullerene cages \( C_n \) (\( n = 20–50 \)) considered in this study. Some of these cages were constructed as feasible cages in our laboratory while the structures for \( C_{20}–C_{36} \) and \( C_{30} \) are the optimized SCF structures as reported by Feyereisen et al. [12]. As seen from fig. 1 we consider two possible fullerene cages for \( C_{40} \) (\( T_d, D_3 \) symmetries). The isomers of the polysubstituted \( C_{60} \) (buckminsterfullerene) were considered before [15]. We use the rotational subgroup uniformly for all cages so that the chiral isomers are also included in our isomer counts.

Table 1 shows the results of our enumeration for the isomers of \( C_{20}H_n \) and \( C_{20}H_nX_m \) for several possible values of \( n \) and \( m \). Since \( C_{20} \) is a high-symmetry icosahedral cage only one isomer is possible for \( C_{20}H \) consistent with our computed value for \( n = 1 \). As seen from table 1 there are 6 isomers for \( C_{20}H_2 \). Among these there is one isomer in which the hydrogen atoms are adjacent. Generally isomers which lead to minimum possible conjugation will be more stable since reduction reactions selectively attack the conjugated bonds [7]. As seen from table 1 there are 21
Table 1
 Enumeration of isomers of C_{20}H_{n} and C_{20}H_{n}F_{m} in the rotational subgroup of the parent cage

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Table 2
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Possible isomers for C_{20}H_{3} are 96 isomers for C_{20}H_{4}.

Enumeration of isomers of C_{20}H_{n}X_{n} is more involved since there are more combinatorial possibilities. As seen from table 2, there are 7 isomers for C_{20}H_{2}HF, 57 isomers for C_{20}H_{2}F, 327 isomers for C_{20}H_{2}F_{2} and so on. Likewise we compute 2586 isomers for C_{20}H_{2}F_{3}. The numbers grow to large but manageable values for other cases even though the cage has a high icosahedral symmetry. The largest number of isomers is computed for C_{20}H_{7}F_{7} which is 2217132.

Table 2 shows our enumeration of the isomers of C_{20}H_{n} and C_{20}H_{n}F_{m}. We used the D_{6} group to enumerate the isomers (see fig. 1). We find two isomers for C_{20}H_{2} suggesting that there are two types of atoms in the C_{20} carbon cage. It can be seen that twelve atoms which constitute the two hexagons in the C_{20} cage (fig. 1) are equivalent but belong to a different equivalence class compared to the atoms which are shared exclusively by pentagons. Hence there are two types of atoms in the C_{20} cage. Likewise there are 30 possible C_{20}H_{2} isomers. Again some C_{n}H_{m} species are likely to be more stable than others. C_{24}H_{n} species which leave one unconjugated double bond per pentagon are likely to be more stable analogous to the unusually stable C_{60}H_{36} observed by Smalley and co-workers [5] through the Birch reduction of the C_{60} buckminsterfullerene. The largest number of isomers is found for C_{24}H_{12} (225898) as expected.

There are in all 23536105821 isomers for C_{24}H_{n}F_{m}. The total isomer count for a given number of substituents measures both the complexity of the cage and the symmetry of the cage. As the symmetry goes up the isomer count goes down for a given fullerene cage. We find 46 isomers for C_{24}H_{2}HF, 506 isomers for C_{24}H_{2}F, 3542 isomers for C_{24}H_{3}F. The maximum isomer count is reached for C_{24}H_{3}F_{8} which is 758812860.
Table 3 shows the computed isomers for C_{26}H_{n} and selected combinations for C_{26}H_{m}F_{n}. The C_{26} cluster which has D_{3h} symmetry gives rise to five isomers for C_{26}H. There are 3 hexagons and 12 pentagons in the C_{26} fullerene cage. Due to the low D_{3} rotational symmetry there are more possible isomers for both C_{26}H_{n} and C_{26}H_{m}F_{n}. Hence we find 61 isomers for C_{26}H, 436 isomers for C_{26}H_{3}, etc. The maximum value of 1733480 is reached for C_{26}H_{13}. The picture for C_{26}H_{n}F_{m} is more complicated as expected. There are 109 isomers for C_{26}HF, 1300 isomers for C_{26}H_{2}F,

9972 isomers for C_{26}H_{3}F. The maximal isomer count is reacted for C_{26}H_{12}F_{3} which is 135207800.

Table 4 shows our computed results for the enumeration of the isomers of C_{28}H_{n}. In this context we point out that Smalley and co-workers [7] have recently synthesized C_{28} fullerene with a tetravalent metal atom inside. The C_{28}H_{4} molecule is consid-

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Table 5

Isomers of C\textsubscript{60}H\textsubscript{24}C\textsubscript{50}H\textsubscript{14} (see fig. 1 for the parent cage)

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tered to be very stable. As seen from table 4 we find 3 isomers for C_{28}H, 24 isomers for C_{28}H_{2}, 161 isomers for C_{28}H_{3}, 928 isomers for C_{28}H_{4}, etc. The maximal count is reached for C_{28}H_{14} which is 1675584. In table 4 we also show selected isomer counts for the C_{28}H_{n}F_{m} isomers. As seen from this table there are 39 isomers for C_{28}HF, 441 isomers for C_{28}H_{2}F, 3513 isomers for C_{28}H_{3}F. The maximal count is reached for C_{28}H_{15}F which is 26584734120.

Table 5 shows the isomer counts for substituted fullerene cages C_{30}C_{50}. For C_{30}H we find 3 isomers if the parent cage has D_{3h} symmetry. There are 51 isomers for C_{30}H_{2}. There maximum number of 14545485 isomers is found for C_{30}H_{14}. The C_{32} cage has a lower D_{3h} symmetry compared to the C_{30} cage. The parent cage for C_{32} is chiral and thus every substituted isomer of C_{32} is chiral. Hence there are 6 C_{32}H isomers and 91 C_{32}H_{2} isomers. The maximum count of 100186668 is reached for C_{32}H_{16}. Due to high symmetry (D_{6h}) the C_{36} cage has fewer isomers for a given number of hydrogen atoms. Thus there are 3 isomers for C_{36}H, 63 isomers for C_{36}H_{2}. The maximum value of 609014886 is reached for C_{36}H_{18}. The C_{38} cage has a somewhat lower C_{5} symmetry. It yields 14 and 235 isomers for the mono- and di-substituted cages. The maximum value of 11781755832 is reached for the C_{38}H_{19} cage.

The C_{40} cage is interesting in that we found at least two different structures with D_{5d} and T_{d} symmetries (fig. 1). These two structures are readily distinguished by their isomer counts. The C_{40} cage with D_{5d} symmetry has larger number of isomers compared to the T_{d} cage. There are 4 and 88 C_{40}H and C_{40}H_{2} isomers with D_{5d} symmetry while the corresponding isomers counts for the T_{d} cage are 3 and 41, respectively. The number of NMR signals of the two cages differ also and thus ^{13}C NMR will readily differentiate these two cages. The maximal isomer count of 13784745288 is reached for the C_{40} cage with D_{5d} symmetry (C_{40}H_{20}). The corresponding count for the T_{d} cage is 5743723334. Hence isomer count facilitates differing cages of different symmetries.

The C_{42} cage possesses only a threefold axis of symmetry and three C_{3} axes resulting in a D_{3h} group. Hence it is interesting that the parent cage itself contains no improper axes of rotation and is thus chiral (fig. 1). Consequently it has much larger isomer counts. There are 7, 154 and 1918 isomers for C_{42}H, C_{42}H_{2} and C_{42}H_{3}, respectively. The maximal value of 89709646884 is reached for the C_{42}H_{21} cluster. The C_{44} cluster has the same rotational subgroup as C_{42}. Hence the isomer counts are larger for the C_{44}H_{n} species as evidenced from table 5. There are 8, 169 and 2212 isomers for C_{44}H, C_{44}H_{2} and C_{44}H_{3}, respectively.

The C_{50} cage considered here (fig. 1) has a D_{3h} point group symmetry. It gives rise to 5, 135 and 1960 isomers for C_{50}H, C_{50}H_{2} and C_{50}H_{3}. The maximal value of 12641060643876 is reached for the C_{50}H_{25} cage. From our isomer counts we predict 5 ^{13}C NMR signals for C_{50}, 7 NMR signals for C_{42} (D_{3h} symmetry) and 3 NMR signals for C_{40} (T_{d} symmetry).

4. Conclusion

In this investigation we systematically enumerated isomers of polysubstituted fullerene cages C_{k} for k=20-50. Isomer counts were computed in quadruple precision arithmetic for both C_{k}H_{n} and C_{k}H_{n}F_{m} compounds. Among the cages considered here the parent cages themselves for C_{32} and C_{42} were chiral and thus all substituted isomers of C_{32} and C_{42} are chiral.

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