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Enumeration of isomers of alkylcyclopropanes by means of alkyl 1,1-biradicals

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Henze and Blair [2] have successfully derived algorithms for enumerating the number of constitutional isomers of aliphatic compounds using alkyl radicals; however, the algorithms cannot be extended to enumerate constitutional isomers of cyclic compounds. Similarly, Read [4] has advocated the use of alkyl biradicals to enumerate constitutional isomers of aliphatic compounds, but not cyclic compounds. Apparently, the use of alkyl biradicals in the enumeration of constitutional isomers of cyclic compounds has been neglected. In this communication, an algorithm using alkyl biradicals to enumerate the number of constitutional isomers of cyclic compounds, namely alkylcyclopropanes, is described.

An alkylcyclopropane with formula C_nH_{2n} is a cyclic compound with a 3-membered ring. In this study, an alkylcyclopropane molecule is considered to be formed by three alkyl biradicals by pairing each one of the unpaired electrons with that of two adjacent alkyl 1,1-biradicals. The three alkyl biradical molecules have carbon content i, j, and k, respectively, where $i + j + k = n$ and i, j, k are positive integers with values $\geqslant 1$. For an alkyl biradical molecule of carbon content m, the number of constitutional isomers is B_m. The number of constitutional isomers of cyclopropane can be enumerated by considering the following three conditions:

Condition 1: $i \neq j \neq k$.

Condition 2: $i \neq j = k$.

Condition 3: $i = j = k$.

For condition 1, the number of constitutional isomers is

$$B_i B_j B_k.$$

For condition 2, the number of constitutional isomers is

$$B_i \left\{ \frac{1}{2} B_j (1 + B_j) \right\} = \frac{1}{2} B_i B_j (1 + B_j).$$

In this condition, the two alkyl biradical molecules are regarded as a single unit (or a new alkyl biradical molecule). The number of constitutional isomers of this new alkyl biradical molecule is

$$B_j + \frac{1}{2}B_j(B_j - 1) = \frac{1}{2}B_j(1 + B_j).$$

For condition 3, the number of constitutional isomers is

$$B_i + B_i(B_i - 1) + \frac{1}{6}B_i(B_i - 1)(B_i - 2).$$

In this condition, the number of constitutional isomers of cyclopropane when the three alkyl biradical molecules are identical is B_i. When only two alkyl biradical molecules are identical (for $B_i \geqslant 2$), the number of constitutional isomers is $B_i(B_i - 1)$, and when all the three alkyl biradical molecules are different (for $B_i \geqslant 3$), the number of constitutional isomers is $C^3_{B_i}$ or $B_i(B_i - 1)(B_i - 2)/6$.

To enumerate the number of constitutional isomers of cyclopropane of carbon content n, we have to firstly partition n into three positive integers, i.e., i, j, k; and then calculate the number of constitutional isomers of each individual combinations of i, j, k by the above equations.

For example, if $n = 6$, we have the following combinations of i, j, k values:

$$1\,1\,4, \qquad 1\,2\,3, \qquad 2\,2\,2.$$

The combination 1 1 4 satisfies condition 2, the combination 1 2 3 satisfies condition 1, and the combination 2 2 2 satisfies condition 3. Thus, the number of constitutional isomers for cyclopropane with carbon content 6 is

$$\begin{aligned}&\frac{1}{2}B_4B_1(1 + B_1) + B_1B_2B_3 + B_2\\ &\quad = \frac{1}{2} \times 3 \times 1 \times (1 + 1) + 1 \times 1 \times 2 + 1 = 3 + 2 + 1 = 6.\end{aligned}$$

The values of B_i are taken from Lam [3].

If $n = 8$, we have the following combinations of i, j, k values:

$$1\,1\,6, \qquad 1\,2\,5, \qquad 1\,3\,4, \qquad 2\,2\,4, \qquad 2\,3\,3.$$

Thus the number of isomers of cyclopropane with carbon content 8 is

$$\begin{aligned}&\frac{1}{2}B_6B_1(1 + B_1) + B_1B_2B_5 + B_1B_3B_4 + \frac{1}{2}B_4B_2(1 + B_2) + \frac{1}{2}B_2B_3(1 + B_3)\\ &\quad = \frac{1}{2} \times 14 \times 1 \times (1 + 1) + 1 \times 1 \times 7 + 1 \times 2 \times 3\\ &\qquad + \frac{1}{2} \times 3 \times 1 \times (1 + 1) + \frac{1}{2} \times 1 \times 2 \times (1 + 2)\\ &\quad = 14 + 7 + 6 + 3 + 3 = 33.\end{aligned}$$

Table 1
Number C_i of constitutional isomers of cyclopropane with n carbon atoms.

n	C_i	n	C_i	n	C_i
3	1	9	83	15	19834
4	1	10	196	16	50872
5	3	11	491	17	131423
6	6	12	1214	18	340763
7	15	13	3068	19	887839
8	33	14	7754	20	2321193

Table 2
Abridged IUPAC names of isomers of alkylcyclopropanes.

n	Abridged IUPAC names
4	Me
5	Et; 1,1-Me_2; 1,2-Me_2
6	Pr; iPr; 1-Et-2-Me; 1-Et-1-Me; 1,1,2-Me_3; 1,2,3-Me_3
7	Bu; iBu; sBu; tBu; 1-Me-2-Pr; 1-Me-1-Pr; 1-Me-2-iPr; 1-Me-1-iPr; 1-Et-1,2-Me_2; 1-Et,2,3-Me_2; 1-Et-2,2-Me_2; 1,1,2,3-Me_4; 1,1,2,2-Me_4; 1,2-$Et_2$1,1-Et_2

The number of constitutional isomers of cyclopropane for $n = 3$–20 is shown in table 1, and the isomers for $n = 4$–7 are indicated in table 2.

By means of Pólya's theorem, substituted constitutional and steric isomers of cycloalkanes had been enumerated earlier by Balaban [1].

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