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Enumeration of isomers of alkylcyclobutadienes by means of alkyl 1,1,1-triradicals

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Previous studies have shown that alkyl 1,1-biradicals could be used to enumerate the constitutional isomers of alkenes [1] and cyclopropanes [2]. In this study, an algorithm of using alkyl 1,1,1-triradicals to enumerate the constitutional isomers of alkylcyclobutadienes is described. An alkylcyclobutadiene molecule is considered to be formed by four alkyl 1,1,1-triradicals by pairing two of the electrons with two of the adjacent alkyl 1,1,1-triradicals, and the remaining unpaired electron with one of the other adjacent alkyl 1,1,1-triradical. This enumeration algorithm showed that the constitutional isomers of the methanol series enumerated by Henze and Blair [3] can be used for enumerating the constitutional isomer of unsaturated cyclic compounds.

KEY WORDS: isomer enumeration, alkylcyclobutadienes, alkyl 1,1,1-triradicals

An alkylcyclobut-1,3-diene molecule with formula C_nH_{2n-4} is a cyclic compound with a 4-membered ring and two conjugated double bonds. In this study, an alkylcyclobutadiene molecule is considered to be formed by four alkyl triradicals by pairing two of the unpaired electrons with two of the adjacent alkyl triradicals, and the remaining unpaired electrons with one of the other adjacent alkyl triradical. The four alkyl triradical molecules have carbon content i, j, k, and l, respectively, where $i + j + k + l = n$ and i, j, k, l are integers with values $\geqslant 1$. For an alkyl triradical molecule of carbon content m, the number of constitutional isomers is L_m. L_m is equal to S_{m-1}, where S_{m-1} denotes the number of constitutional isomers of an alkyl group with $m - 1$ carbons. The constitutional isomers of alkylcyclobut-1,3-diene may be partitioned into five classes satisfying the following conditions:

Condition 1. All 4 radicals having different carbon number: $i \neq j$, $i \neq k$, $i \neq l$, $j \neq k$, $j \neq l$, and $k \neq l$.

Condition 2. Exactly 2 radicals having the same carbon number: $i \neq j$, $i \neq k$, $j \neq k$, and $k = l$.

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Condition 3. Exactly 2 radicals having the same carbon number, and the other 2 radicals also having the same carbon number but different from that of the other pair: $i = j$, $k = l$, and $i \neq k$.

Condition 4. Exactly 3 radicals having the same carbon number: $i = j = k \neq l$.

Condition 5. All 4 radicals having the same carbon number: $i = j = k = l$.

For condition 1, the number of constitutional isomers is

$$3L_i L_j L_k L_l.$$

In this condition, the number of isomers of alkylcyclobut-1,3-diene for one spatial combination of the four radicals in the ring is $L_i L_j L_k L_l$. Because there are three possible spatial combinations, the number of constitutional isomers is $3L_i L_j L_k L_l$.

For condition 2, the number of isomers of the pair, i.e., $L_k = L_l$, is

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

and we have two possible spatial combinations of the four radicals in the ring, i.e., either a diagonal pair or an adjacent pair. Thus, the total number of constitutional isomers is:

$$2L_i L_j \left\{\frac{1}{2}L_k(1 + L_k)\right\} = L_i L_j L_k(1 + L_k).$$

For condition 3, we have two spatial combinations of the four radicals in the ring, i.e., either two diagonal pairs or two adjacent pairs. Thus, the number of constitutional isomers is:

$$2 \cdot \frac{1}{2}L_j(1 + L_j) \cdot \frac{1}{2}L_k(1 + L_k) = \frac{1}{2}L_j L_k(1 + L_j)(1 + L_k).$$

For condition 4, the number of constitutional isomers is:

$$\begin{aligned} &L_i L_l + 2 \cdot L_l \cdot L_i(L_i - 1) + 3 \cdot L_l \cdot \frac{1}{6}(L_i)(L_i - 1)(L_i - 2) \\ &= L_i L_l + 2L_l L_i(L_i - 1) + \frac{1}{2}L_l L_i(L_i - 1)(L_i - 2). \end{aligned}$$

The first term of the equation is the number of constitutional isomers when the three radical molecules with the same carbon number are identical. The second term is the number of constitutional isomers when only two of the three radical molecules with the same carbon number are identical and we have two possible spatial combinations of the four radicals in the ring in this subcondition. The third term is the number of constitutional isomers when the three radical molecules with the same carbon number are different and we have three possible spatial combinations of the four radicals in the ring in this subcondition.

For condition 5, the number of constitutional isomers is:

$$L_i + L_i(L_i - 1) + 2 \cdot \frac{1}{2} L_i(L_i - 1) + 2 \cdot \frac{1}{2} \cdot L_i \cdot (L_i - 1) \cdot (L_i - 2) + 3 \cdot \binom{L_i}{4}$$
$$= L_i + 2L_i(L_i - 1) + L_i(L_i - 1)(L_i - 2) + \frac{1}{8} L_i(L_i - 1)(L_i - 2)(L_i - 3).$$

The first term of the equation is the number of constitutional isomers when the four radical molecules are identical. The second term is the number of constitutional isomers when only three of the four radical molecules are identical and we have only one possible spatial combination of the four radicals in the ring in this subcondition. The third term is the number of constitutional isomers when two radicals are identical, and the other two radicals are also identical but the two pairs are different from each other and we have two possible spatial combinations of the four radicals in the ring in this subcondition. The fourth term is the number of constitutional isomers when there is only one pair of identical radical molecules and we have two possible spatial combinations of the four radicals in the ring in this subcondition. The fifth term is the number of constitutional isomers when there are no identical radical molecules and we have three possible spatial combinations of the four radicals in the ring in this subcondition.

To enumerate the number of constitutional isomers of alkylcyclobutadiene of carbon content n, we have to first partition n into four positive integers, i.e., i, j, k, l; and then calculate the number of constitutional isomers of each individual combination of i, j, k, l by the above equations.

For example: if $n = 8$, we have the following combination of i, j, k, l values:

1 1 1 5
1 1 2 4
1 1 3 3
1 2 2 3
2 2 2 2

The combination, 1, 1, 1, 5 satisfies condition 4; the combination 1, 1, 2, 4 satisfies condition 2; the combination, 1, 1, 3, 3 satisfies condition 3; the combination 1, 2, 2, 3 satisfies condition 2; and the combination 2, 2, 2, 2 satisfies condition 5. Thus the number of constitutional isomers for alkylcyclobut-1,3-dienes with 8 carbons is:

$$L_5 + L_2L_4L_1(1 + L_1) + \frac{1}{2} L_1L_3(1 + L_1)(1 + L_3) + L_1L_3L_2(1 + L_2) + 1$$
$$= S_4 + S_1S_3L_1(1 + L_1) + \frac{1}{2} L_1S_2(1 + L_1)(1 + S_2) + L_1S_2S_1(1 + S_1) + 1$$
$$= 4 + 1 \cdot 2 \cdot 1 \cdot (1 + 1) + \frac{1}{2} \cdot 1 \cdot 1 \cdot (1 + 1)(1 + 1) + 1 \cdot 1 \cdot 1 \cdot (1 + 1) + 1$$
$$= 4 + 4 + 2 + 2 + 1$$
$$= 13.$$

Table 1
Number of constitutional isomers of alkylcyclobutadienes.

n	No. of isomers
4	1
5	1
6	3
7	5
8	13
9	26
10	66
11	152
12	366
13	907
14	2225
15	6864

The values of S_n are taken from the paper of Henze and Blair [3].

If $n = 16$, we have the following combination of i, j, k, l values and conditions:

Combination	Condition	No. of isomers	Combination	Condition	No. of isomers
1 1 1 13	4	3057	1 3 5 7	1	204
1 1 2 12	2	2476	1 3 6 6	2	72
1 1 3 11	2	1014	1 4 4 7	2	102
1 1 4 10	2	844	1 4 5 6	1	192
1 1 5 9	2	712	2 2 2 10	4	211
1 1 6 8	2	624	2 2 3 9	2	178
1 1 7 7	3	306	2 2 4 8	2	156
1 2 2 11	2	1014	2 2 5 7	2	136
1 2 3 10	1	633	2 2 6 6	3	72
1 2 4 9	1	534	3 3 3 7	4	17
1 2 5 8	1	468	3 3 4 6	2	32
1 2 6 7	1	408	3 3 5 5	3	20
1 3 3 9	2	178	4 4 4 4	5	6
1 3 4 8	1	234			

Thus, the number of isomers of alkylcyclobutadiene with 16 carbons is 13900. The results also can be obtained by Pólya's theorem [4,5]. For alkylcyclobutadienes with 4 to 15 carbons, the number is shown in table 1.

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