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Note

A mathematical relationship between the number of isomers of alkenes and alkynes: a result established from the enumeration of isomers of alkenes from alkyl biradicals

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A simple and fast algorithm for enumerating alkene isomers is described. This algorithm is based on a 2-step hypothetical chemical reaction. In the first step, an alkane molecule loses two protons becoming an alkyl biradical. In the second step, two alkyl biradicals react to form an alkene molecule. By using two sequential recursive algorithms, the number of computational terms in the enumeration process is much less than when using the Henze–Blair algorithm. By using this simple algorithm, the numbers of constitutional isomers of alkenes and alkynes for carbon content greater than 30 are easily enumerated. In addition, through this algorithm, a mathematical relationship between the number of constitutional isomers of alkenes and alkynes has been established for the first time.

Henze and Blair have developed a number of recursive algorithms for enumerating the constitutional isomers of alkanes [4] and related acyclic structures [6]. One of these recursive algorithms calculated the number of constitutional isomers of alkenes derived from alkyl alcohols [5]. However, the number of computational terms for enumeration of alkenes increased exponentially with the carbon content, e.g., 249 terms for carbon content 30 and 551 terms for carbon content 40. Besides requiring tedious and cumbersome calculation, this algorithm is prone to making errors by manual calculation [5,6]. Here, a simple and fast recursive algorithm has been developed and the result can be easily obtained. In addition, a mathematical relationship between the number of constitutional isomers of alkenes and alkynes has been established for the first time.

The present approach is based on the formation of alkyl biradicals [9]. These alkyl biradicals can be imagined to be formed by a hypothetical chemical reaction in which an alkane molecule loses two protons and becomes an alkyl biradical, i.e., with two unpaired electrons. Interestingly, not all possible alkane isomers are required to form all possible alkyl biradicals as one alkane molecule has many different sites where

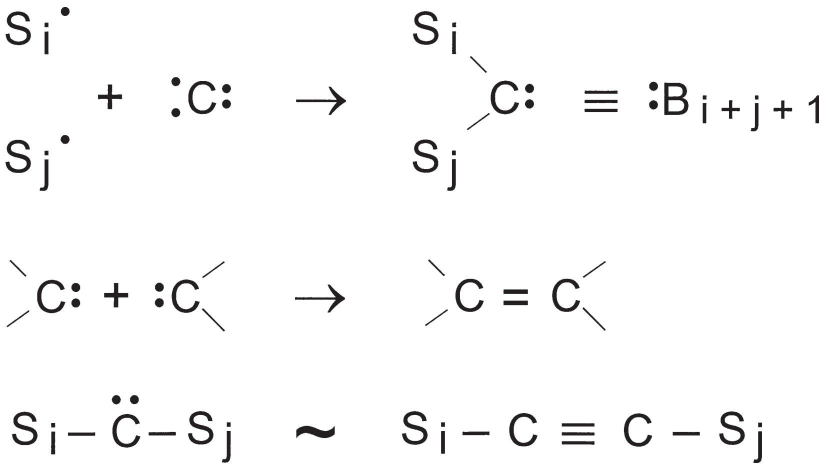

Figure 1. *Top*: mechanism by which an alkyl biradical is formed; *Middle*: two alkyl biradicals combine to form an alkene molecule; *Bottom*: note the marked similarity between the constitutional isomers of alkyl biradicals and alkynes.

the two protons can be lost. When a single alkyl biradical combines with another alkyl biradical, the four electrons will be paired up and form a double bond. The reaction is depicted in figure 1. If an alkyl biradical has k carbons, S_i and S_j denote the number of constitutional isomers of the two alkyl groups with i and j carbons, respectively, and B_k denotes the total number of constitutional isomers of the alkyl biradical of carbon content k, where $k = i + j + 1$, we will have

$$B_k = S_0 \cdot S_{k-1} + S_1 \cdot S_{k-2} + \cdots + S_{(k/2)-1} \cdot S_{k/2} \quad \text{when } k \text{ is even,}$$

or

$$B_k = S_0 \cdot S_{k-1} + S_1 \cdot S_{k-2} + \cdots + (1/2) \cdot S_{(k-1)/2} \cdot (S_{(k-1)/2} + 1) \quad \text{when } k \text{ is odd.}$$

For example, if k is equal to 10,

$$\begin{aligned} B_{10} &= S_0 \cdot S_9 + S_1 \cdot S_8 + S_2 \cdot S_7 + S_3 \cdot S_6 + S_4 \cdot S_5 \\ &= 1 \cdot 211 + 1 \cdot 89 + 1 \cdot 39 + 2 \cdot 17 + 4 \cdot 8 \\ &= 211 + 89 + 39 + 34 + 32 \\ &= 405. \end{aligned}$$

If k is equal to 11,

$$\begin{aligned} B_{11} &= S_0 \cdot S_{10} + S_1 \cdot S_9 + S_2 \cdot S_8 + S_3 \cdot S_7 + S_4 \cdot S_6 + (1/2) \cdot S_5 \cdot (S_5 + 1) \\ &= 1 \cdot 507 + 1 \cdot 211 + 1 \cdot 89 + 2 \cdot 39 + 4 \cdot 17 + (1/2) \cdot 8 \cdot 9 \\ &= 507 + 211 + 89 + 78 + 68 + 36 \\ &= 989. \end{aligned}$$

All the S_i values are taken from papers of Henze and Blair [3], Perry [8], Davis et al. [2] and Trinajstic [10]. The results, generated from a computer program which calculates all B_i values from $i = 1$ to 32 and B_i values from $i = 33$ to 50 calculated by *Mathematica*™, are shown in table 1.

Table 1
Number of constitutional isomers of alkyl biradicals, alkynes and alkenes.

n	$B_i = T_{i+1}$	E_i
1	1	
2	1	1
3	2	1
4	3	3
5	7	5
6	14	13
7	32	27
8	72	66
9	171	153
10	405	377
11	989	914
12	2 426	2 281
13	6 045	5 690
14	15 167	14 397
15	38 422	36 564
16	97 925	93 650
17	251 275	240 916
18	648 061	623 338
19	1 679 869	1 619 346
20	4 372 872	4 224 993
21	11 428 365	11 062 046
22	29 972 078	29 062 341
23	78 859 809	76 581 151
24	208 094 977	202 365 823
25	550 603 722	536 113 477
26	1 460 457 242	1 423 665 699
27	3 882 682 803	3 788 843 391
28	10 344 102 122	10 103 901 486
29	27 612 603 765	26 995 498 151
30	73 844 151 259	72 253 682 560
31	197 818 389 539	193 706 542 776
32	530 775 701 520	520 115 491 654
33	1 426 284 383 289	1 398 573 129 520
34	3 838 066 701 350	3 765 852 863 965
35	10 341 758 769 406	10 153 132 533 267
36	27 900 947 721 908	27 407 165 417 067
37	75 362 644 825 968	74 067 347 237 840
38	203 787 850 635 992	200 383 361 535 700
39	551 645 375 673 949	542 680 628 199 354
40	1 494 781 478 155 753	1 471 134 003 594 656

Table 1
(Continued.)

n	$B_i = T_{i+1}$	E_i
41	4 054 242 571 711 886	3 991 760 770 564 545
42	11 006 161 817 116 528	10 840 810 373 009 111
43	29 904 564 722 290 758	29 466 321 827 521 532
44	81 319 947 893 937 569	80 156 778 216 023 220
45	221 308 699 013 145 314	218 217 238 001 308 458
46	602 735 147 429 051 222	594 507 985 135 689 828
47	1 642 733 167 881 428 721	1 620 811 333 794 745 303
48	4 480 296 443 626 480 469	4 421 814 637 212 588 436
49	12 227 375 730 982 990 115	12 071 183 364 508 399 476
50	33 391 418 880 319 176 319	32 973 806 480 104 397 769

n: number of carbon; B_i: number of constitutional isomers of an alkyl biradical with i carbon atoms; T_{i+1}: number of constitutional isomers of an alkyne molecule with $i+1$ carbon atoms; E_i: number of constitutional isomers of an alkene with i carbon atoms.

Now, we will use these alkyl biradicals to synthesize alkenes by combining two alkyl biradicals (figure 1). In this model, both *cis*- and *trans*-alkenes have equal chances to be formed. Using the same type of recursive algorithm as above, for an alkene molecule containing k carbon atoms, the number of constitutional isomers, E_k, is equal to

$$E_k = B_1 \cdot B_{k-1} + B_2 \cdot B_{k-2} + B_3 \cdot B_{k-3} + \cdots + (1/2) \cdot B_{k/2} \cdot (B_{k/2} + 1) \quad \text{when } k \text{ is even,}$$

or

$$E_k = B_1 \cdot B_{k-1} + B_2 \cdot B_{k-2} + B_3 \cdot B_{k-3} + \cdots + B_{(k-1)/2} \cdot B_{(k+1)/2} \quad \text{when } k \text{ is odd.}$$

For example, if k is equal to 13,

$$\begin{aligned} E_{13} &= B_1 \cdot B_{12} + B_2 \cdot B_{11} + B_3 \cdot B_{10} + B_4 \cdot B_9 + B_5 \cdot B_8 + B_6 \cdot B_7 \\ &= 1 \cdot 2426 + 1 \cdot 989 + 2 \cdot 405 + 3 \cdot 171 + 7 \cdot 72 + 14 \cdot 32 \\ &= 2426 + 989 + 810 + 513 + 504 + 448 \\ &= 5690. \end{aligned}$$

If k is equal to 14,

$$\begin{aligned} E_{14} &= B_1 \cdot B_{13} + B_2 \cdot B_{12} + B_3 \cdot B_{11} + B_4 \cdot B_{10} + B_5 \cdot B_9 + B_6 \cdot B_8 \\ &\quad + (1/2) \cdot B_7 \cdot (B_7 + 1) \\ &= 1 \cdot 6045 + 1 \cdot 2426 + 2 \cdot 989 + 3 \cdot 405 + 7 \cdot 171 + 14 \cdot 72 + (1/2) \cdot 32 \cdot 33 \\ &= 6045 + 2426 + 1978 + 1215 + 1197 + 1008 + 528 \\ &= 14397. \end{aligned}$$

Alternatively, the above equations can be written in matrix form as a single matrix equation:

$$\begin{pmatrix} B_2 & 0 & 0 & \dots\dots & \dots & 0 & 0 \\ B_4 & B_3 & 0 & \dots\dots & \dots & 0 & 0 \\ B_6 & B_5 & B_4 & 0\ \dots & \dots & 0 & 0 \\ & & & \vdots\ \ 0 & \dots & \dots & 0 \\ & & & \vdots & 0 & \dots & 0 \\ & & & \vdots & & & \\ B_{k-3} & B_{k-4} & B_{k-5} & \dots\dots & B_{(k+1)/2} & B_{(k-1)/2} & 0 \\ B_{k-1} & B_{k-2} & B_{k-3} & \dots\dots & \dots & B_{(k+3)/2} & B_{(k+1)/2} \end{pmatrix} \begin{pmatrix} B_1 \\ B_2 \\ B_3 \\ \vdots \\ \vdots \\ \vdots \\ B_{(k-3)/2} \\ B_{(k-1)/2} \end{pmatrix} = \begin{pmatrix} E_3 \\ E_5 \\ E_7 \\ \vdots \\ \vdots \\ \vdots \\ E_{k-2} \\ E_k \end{pmatrix}$$

when k is odd, or

$$\begin{pmatrix} \frac{1}{2}(B_1+1) & 0 & 0 & \dots\dots & \dots & 0 & 0 \\ B_3 & \frac{1}{2}(B_2+1) & 0 & \dots\dots & \dots & 0 & 0 \\ B_5 & B_4 & \frac{1}{2}(B_3+1) & 0\ \dots & \dots & 0 & 0 \\ & & & \vdots\ \ 0 & \dots & \dots & 0 \\ & & & \vdots & 0 & \dots & 0 \\ & & & \vdots & & & \\ B_{k-3} & B_{k-4} & B_{k-5} & \dots\dots & B_{k/2} & \frac{1}{2}(B_{(k-2)/2}+1) & 0 \\ B_{k-1} & B_{k-2} & B_{k-3} & \dots\dots & B_{(k+4)/2} & B_{(k+2)/2} & \frac{1}{2}(B_{k/2}+1) \end{pmatrix}$$

$$\times \begin{pmatrix} B_1 \\ B_2 \\ B_3 \\ \vdots \\ \vdots \\ \vdots \\ B_{(k-2)/2} \\ B_{k/2} \end{pmatrix} = \begin{pmatrix} E_2 \\ E_4 \\ E_6 \\ \vdots \\ \vdots \\ \vdots \\ E_{k-2} \\ E_k \end{pmatrix}$$

when k is even.

For example, if $k = 13$,

$$\begin{pmatrix} B_2 & 0 & 0 & 0 & 0 & 0 \\ B_4 & B_3 & 0 & 0 & 0 & 0 \\ B_6 & B_5 & B_4 & 0 & 0 & 0 \\ B_8 & B_7 & B_6 & B_5 & 0 & 0 \\ B_{10} & B_9 & B_8 & B_7 & B_6 & 0 \\ B_{12} & B_{11} & B_{10} & B_9 & B_8 & B_7 \end{pmatrix} \begin{pmatrix} B_1 \\ B_2 \\ B_3 \\ B_4 \\ B_5 \\ B_6 \end{pmatrix} = \begin{pmatrix} E_3 \\ E_5 \\ E_7 \\ E_9 \\ E_{11} \\ E_{13} \end{pmatrix},$$

or if $k = 12$,

$$\begin{pmatrix} \frac{1}{2}(B_1+1) & 0 & 0 & 0 & 0 & 0 \\ B_3 & \frac{1}{2}(B_2+1) & 0 & 0 & 0 & 0 \\ B_5 & B_4 & \frac{1}{2}(B_3+1) & 0 & 0 & 0 \\ B_7 & B_6 & B_5 & \frac{1}{2}(B_4+1) & 0 & 0 \\ B_9 & B_8 & B_7 & B_6 & \frac{1}{2}(B_5+1) & 0 \\ B_{11} & B_{10} & B_9 & B_8 & B_7 & \frac{1}{2}(B_6+1) \end{pmatrix}$$

$$\times \begin{pmatrix} B_1 \\ B_2 \\ B_3 \\ B_4 \\ B_5 \\ B_6 \end{pmatrix} = \begin{pmatrix} E_2 \\ E_4 \\ E_6 \\ E_8 \\ E_{10} \\ E_{12} \end{pmatrix}.$$

In this model, the number of terms for any alkene is one as compared to 249 terms for E_{30} and 551 terms for E_{40} using the Henze–Blair algorithm. The number of constitutional isomers, E_k, from $k = 2$ to 50, is shown in table 1. All the results, for $k = 2$ to 30, are identical to that of Henze and Blair [5], and the results for $k = 31$ to 50, are identical to that of Knop et al. [7]. A computer program written in Pascal is available on request.

It is interesting to note that B_k is equivalent to T_{k+1} of the alkyne series [1], where T_k is the number of constitutional isomers of an alkyne molecule of carbon content k. This is not unexpected as both isomers of the two homologous series are enumerated from alkyl alcohols by the same algorithm, but differing by one carbon atom. A mathematical relationship can be established between the number of isomers of alkenes and alkynes by substituting T_{k+1} for B_k in the above equations. We have

$$E_k = T_2 \cdot T_k + T_3 \cdot T_{k-1} + T_4 \cdot T_{k-2} + \cdots + (1/2) \cdot T_{(k+2)/2} \cdot (T_{(k+2)/2} + 1) \quad \text{when } k \text{ is even},$$

or

$$E_k = T_2 \cdot T_k + T_3 \cdot T_{k-1} + T_4 \cdot T_{k-2} + \cdots + T_{(k+1)/2} \cdot T_{(k+3)/2} \quad \text{when } k \text{ is odd}.$$

Finally, we can use a matrix equation to describe the relationship between the number of constitutional isomers of alkynes and alkenes. We have

$$
\begin{pmatrix}
T_3 & 0 & 0 & \ldots & \ldots & \ldots & 0 & 0 \\
T_5 & T_4 & 0 & \ldots & \ldots & \ldots & 0 & 0 \\
T_7 & T_6 & T_5 & 0 & \ldots & \ldots & 0 & 0 \\
 & & & \vdots & 0 & \ldots & \ldots & 0 \\
 & & & \vdots & & 0 & \ldots & 0 \\
 & & & \vdots & & & & \\
T_{k-2} & T_{k-3} & T_{k-4} & \ldots & \ldots & T_{(k+3)/2} & T_{(k+1)/2} & 0 \\
T_k & T_{k-1} & T_{k-2} & \ldots & \ldots & \ldots & T_{(k+5)/2} & T_{(k+3)/2}
\end{pmatrix}
\begin{pmatrix}
T_2 \\ T_3 \\ T_4 \\ \vdots \\ \vdots \\ \vdots \\ T_{(k-1)/2} \\ T_{(k+1)/2}
\end{pmatrix}
=
\begin{pmatrix}
E_3 \\ E_5 \\ E_7 \\ \vdots \\ \vdots \\ \vdots \\ E_{k-2} \\ E_k
\end{pmatrix}
$$

when k is odd, or

$$
\begin{pmatrix}
\frac{1}{2}(T_2+1) & 0 & 0 & \ldots & \ldots & 0 & 0 \\
T_4 & \frac{1}{2}(T_3+1) & 0 & \ldots & \ldots & 0 & 0 \\
T_6 & T_5 & \frac{1}{2}(T_4+1) & 0 \ \ldots & \ldots & 0 & 0 \\
 & & & \vdots \ \ 0 & \ldots & 0 & 0 \\
 & & & \vdots & 0 & \ldots & 0 \\
 & & & \vdots & & & \\
T_{k-2} & T_{k-3} & T_{k-4} & \ldots & T_{(k+2)/2} & \frac{1}{2}(T_k+1) & 0 \\
T_k & T_{k-1} & T_{k-2} & \ldots & T_{(k+6)/2} & T_{(k+4)/2} & \frac{1}{2}(T_{(k+2)/2}+1)
\end{pmatrix}
$$

$$
\times
\begin{pmatrix}
T_2 \\ T_3 \\ T_4 \\ \vdots \\ \vdots \\ \vdots \\ T_k \\ T_{(k+2)/2}
\end{pmatrix}
=
\begin{pmatrix}
E_2 \\ E_4 \\ E_6 \\ \vdots \\ \vdots \\ \vdots \\ E_{k-2} \\ E_k
\end{pmatrix}
$$

when k is even.

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