

The Number of Isomeric Aliphatic Hydrocarbons

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From time to time papers dealing with the problem of calculating the number of isomeric aliphatic hydrocarbons have been published. In the present paper recursion formulas for the calculation of isomeric hydrocarbons of the acetylene series and the ethylene series — with and without taking into consideration stereoisomerism — will be derived. These formulas presuppose the knowledge of the number of isomeric univalent radicals of the methane series, and these numbers are therefore mentioned in the sections I A and II A. The new formulas have been arrived at in I B, I C, II B and II C.

SYMBOLS USED IN THE PRESENT PAPER

| | | |
|--|---|--|
| n | = the number of carbon atoms in a hydrocarbon molecule. | |
| R_n | = the radical C_nH_{2n+1} . | |
| p_n | = the number of isomeric primary radicals R_n | } without taking stereoisomerism into account. |
| s_n | = » » » secondary » R_n | |
| t_n | = » » » tertiary » R_n | |
| T_n | = » » » radicals R_n | |
| A_n | = » » » alkanes C_nH_{2n+2} | |
| E_n | = » » » alkenes C_nH_{2n} | |
| I_n | = » » » alkynes C_nH_{2n-2} | } |
| I'_n | = » » » stereoisomeric + non-stereoisomeric alkynes. | |
| $I(s)_n$ | = » » » » alkynes. | |
| $I(ns)_n$ | = » » » non-stereoisomeric alkynes. | |
| $E'_n, E(s)_n, E(ns)_n; p'_n, p(s)_n, p(ns)_n; etc.$ are defined in the same manner. | | |
| $a, b, c, d, g, h, i, j, x$ and y are integers > 0 . | | |

In many of the following formulas certain terms have to be left out for special values of n . It turns out that this happens for such values of n for

which the subscripts in the terms are fractions: *E. g.* in formula (2) the last term should be left out for such values of n for which the subscript $\frac{n-1}{2}$ is a fraction; that is for all even values of n . This is indicated in the formula by applying the factor λ to the last term. λ is in other words a function of n . It takes the values 1 or 0, according as the subscripts in the term to which λ is applied are integers or not.

I. STEREOISOMERISM NOT CONSIDERED

A. Hydrocarbons of the methane series (alkanes). In 1875 Cayley¹ tried to derive a formula by which the number of isomeric alkanes C_nH_{2n+2} could be calculated, and later on several attempts have been made to solve the problem (the literature until 1931 is reviewed by Henze and Blair^{2, 3}). In 1931 Henze and Blair³ succeeded in solving the problem by first deriving recursion formulas for the number of isomeric alcohols R_nOH classified in primary, secondary and tertiary alcohols².

From the definition of p_n , s_n , t_n and T_n it follows that

$$T_n = p_n + s_n + t_n$$

Henze and Blair found *):

$$p_n = T_{n-1} \quad (1)$$

$$\text{and} \quad s_n = \sum T_a \cdot T_b + \lambda \cdot \frac{1}{2} \cdot T_{\frac{n-1}{2}} \cdot (T_{\frac{n-1}{2}} + 1) \quad (2)$$

$$\begin{aligned} a &< b \\ a + b &= n - 1 \end{aligned}$$

and they also found a formula for t_n , which is of no interest for this paper. Using these formulas and the value $T_1 = 1$ it was possible to compute T_2 , T_3 , T_4 , ... Henze and Blair thereafter gave direction for computing A_{2n} using the values of T_1 , T_2 , ... T_n and for computing A_{2n+1} using the values of T_1 , T_2 , ... T_{n+1} .

Using Henze and Blairs' formulas the numerical values of T_n , p_n , s_n and t_n for $n \leq 30$ were published^{2, 4}, and the numerical values of A_n for $n \leq 40$ and for $n = 60$ were also published^{3, 4, 5}.

* These and later formulas by Henze and Blair or others are here expressed in a more concise form than in the original papers.

B. Hydrocarbons of the acetylene series (alkynes). Coffman, Blair and Henze ⁶ have calculated the number of isomeric alkynes. They considered $R-C\equiv C-R'$, where at first they assumed R to represent a hydrogen atom and at the same time R' an arbitrary radical R_{n-2} . Afterwards they assumed R and R' to represent two radicals R_i and R_j , where $i < j$ and $i + j = n - 2$. The three authors found:

$$I_n = T_{n-2} + \sum_{\substack{i < j \\ i + j = n - 2}} T_i \cdot T_j + \lambda \cdot \frac{1}{2} \cdot T_{\frac{n-2}{2}} \cdot (T_{\frac{n-2}{2}} + 1) \quad (3)$$

However, this formula can be rewritten by means of (1):

$$I_n = p_{n-1} + \sum_{\substack{1 < g < h \\ g + h = n}} p_g \cdot p_h + \lambda \cdot \frac{1}{2} \cdot p_{\frac{n}{2}} \cdot (p_{\frac{n}{2}} + 1)$$

and using

$$p_{n-1} = p_1 \cdot p_{n-1}$$

we get:

$$I_n = \sum_{\substack{g < h \\ g + h = n}} p_g \cdot p_h + \lambda \cdot \frac{1}{2} \cdot p_{\frac{n}{2}} \cdot (p_{\frac{n}{2}} + 1) \quad (4)$$

The formula (4) may be derived directly from the following consideration. An alkyne may be considered as consisting of two primary radicals R_g and R_h , in which two hydrogen atoms are removed from the primary carbon atom in R_g as well as in R_h , and thereafter the two resulting tervalent radicals are joined in a triple bond. This gives for n odd:

$$I_n = p_1 \cdot p_{n-1} + p_2 \cdot p_{n-2} + \dots + \frac{p_{n-1}}{2} \cdot \frac{p_{n+1}}{2} \quad (4a)$$

and for n even:

$$I_n = p_1 \cdot p_{n-1} + p_2 \cdot p_{n-2} + \dots + \frac{p_{n-2}}{2} \cdot \frac{p_{n+2}}{2} + \frac{1}{2} \cdot p_{\frac{n}{2}} \cdot (p_{\frac{n}{2}} + 1) \quad (4b)$$

The content of (4a) and (4b) is included in (4).

However, formula (4) can be further simplified. From (2) it follows that

$$s_{n-1} = \sum_{\substack{i < j \\ i+j=n-2}} T_i \cdot T_j + \lambda \cdot \frac{1}{2} \cdot T_{\frac{n-2}{2}} (T_{\frac{n-2}{2}} + 1)$$

and using (1) we get:

$$s_{n-1} = \sum_{\substack{1 < g < h \\ g+h=n}} p_g \cdot p_h + \lambda \cdot \frac{1}{2} \cdot p_{\frac{n}{2}} \cdot (p_{\frac{n}{2}} + 1)$$

or since

$$p_1 \cdot p_{n-1} = p_{n-1}$$

we get:

$$s_{n-1} = -p_{n-1} + \sum_{\substack{g < h \\ g+h=n}} p_g \cdot p_h + \lambda \cdot \frac{1}{2} \cdot p_{\frac{n}{2}} \cdot (p_{\frac{n}{2}} + 1)$$

which compared with (4) gives:

$$I_n = p_{n-1} + s_{n-1} \quad (5)$$

Formula (5) may also be derived in the following manner. In the isomeric alkynes C_nH_{2n-2} α) a terminal carbon atom takes part in the triple bond, or β) no terminal carbon atom takes part in the triple bond. Alkynes of type α may be derived from the primary radicals R_{n-1} by removing two hydrogen atoms from the primary carbon atom, and thereafter attaching the resulting tervalent radical to $\equiv C-H$; this procedure results in p_{n-1} different alkynes. Alkynes of type β may be derived from the secondary radicals R_{n-1} by removing the hydrogen atom and the radical R_a from $\begin{array}{c} R_a \\ \diagdown \\ C \\ \diagup \\ R_b \end{array} \begin{array}{c} H \\ \diagup \\ C \\ \diagdown \end{array}$, and thereafter attaching the resulting tervalent radical to $\equiv C-R_a$; this procedure results in s_{n-1} different alkynes.

Numerical values (found in literature ⁶) of I_n for $n \leq 30$ are checked by means of formula (5).

C. *Hydrocarbons of the ethylene series (alkenes)*. Henze and Blair⁷ have calculated the number of isomeric alkenes. They divided the problem into four parts, in accordance with the fact that all alkenes may be considered as derived from $\text{H}_2\text{C}=\text{CH}_2$ by substituting 1, 2, 3 or 4 hydrogen atoms by suitable radicals. In this manner the authors found a rather complicated method for calculating E_n , a method which may be carried through when T_x is known for $x \leq n-2$.

However, a simple formula may be derived in a very direct manner as follows. We may think of an alkene as a hydrocarbon built up in the following way. From a primary or secondary radical R_g a hydrogen atom is removed from the primary or secondary carbon atom; and the same is done in the primary or secondary radical R_h . By joining the two resulting bivalent radicals in a double bond an alkene is produced. From this it follows that

$$E_n = \sum_{\substack{g < h \\ g + h = n}} (p_g + s_g) \cdot (p_h + s_h) + \lambda \cdot \frac{1}{2} \cdot (p_{\frac{n}{2}} + s_{\frac{n}{2}}) \cdot (p_{\frac{n}{2}} + s_{\frac{n}{2}} + 1) \quad (6)$$

which by means of (5) can be rewritten as:

$$E_n = \sum_{\substack{1 < a < b \\ a + b = n + 2}} I_a \cdot I_b + \lambda \cdot \frac{1}{2} \cdot I_{\frac{n+2}{2}} \cdot (I_{\frac{n+2}{2}} + 1) \quad (7)$$

Numerical values (found in literature^{7, 8}) of E_n for $n \leq 20$ are checked by means of formula (7), and the following values are calculated for $n \leq 30$ (Table 1).

Table 1. The number, E_n , of isomeric alkenes (not considering stereoisomerism) with n carbon atoms ($20 < n \leq 30$).

| n | E_n | n | E_n |
|-----|-------------|-----|----------------|
| 21 | 11 062 046 | 26 | 1 423 665 699 |
| 22 | 29 062 341 | 27 | 3 788 843 391 |
| 23 | 76 581 151 | 28 | 10 103 901 486 |
| 24 | 202 365 823 | 29 | 26 995 498 151 |
| 25 | 536 113 477 | 30 | 72 253 682 560 |

II. STEREOISOMERISM CONSIDERED

A. Alkanes. Blair and Henze have derived formulas for computing stereoisomeric and non-stereoisomeric primary, secondary and tertiary radicals⁹ and thereafter formulas for computing stereoisomeric and non-stereoisomeric alkanes¹⁰. The chain of reasoning was analogous to that used by the authors in the case where stereoisomerism was not taken into account^{2, 3}, but the computations were for good reasons more complicated. The authors published¹¹ the numerical values for T'_n , $T(s)_n$, $T(ns)_n$; $p(s)_n$, $p(ns)_n$; $s(s)_n$, $s(ns)_n$; $t(s)_n$, $t(ns)_n$ for $n \leq 20$; and also¹² for A'_n , $A(s)_n$, $A(ns)_n$ for $n \leq 20$.

The following formulas taken from Blair and Henze are of interest for this paper:

$$p'_n = T'_{n-1} \quad (8a)$$

$$p(ns)_n = T(ns)_{n-1} \quad (8b)$$

$$s'_n = 2 \cdot \sum T'_a \cdot T'_b + \lambda \cdot (T'_{\frac{n-1}{2}})^2 \quad \text{for } n > 1 \quad (9)$$

$$a < b$$

$$a + b = n-1$$

B. Alkines. Coffman¹¹ has calculated the number of stereoisomeric and non-stereoisomeric alkines. The chain of reasoning was (apart from the fact that it was more complicated) the same as by Coffman, Blair and Henze⁶, where stereoisomerism was not taken into account.

However, the considerations can be carried through in a more straightforward manner if the method which led to the formula (4) is used. No stereoisomerism is destroyed through joining two tervalent radicals, and therefore the following must be true:

$$I'_n = \sum p'_g \cdot p'_h + \lambda \cdot \frac{1}{2} \cdot p'_{\frac{n}{2}} \cdot (p'_{\frac{n}{2}} + 1) \quad (10)$$

$$g < h$$

$$g + h = n$$

A non-stereoisomeric alkine must necessarily be derived from two non-stereoisomeric radicals, and therefore we have:

$$I(ns)_n = \sum p(ns)_g \cdot p(ns)_h + \lambda \cdot \frac{1}{2} \cdot p(ns)_{\frac{n}{2}} \cdot (p(ns)_{\frac{n}{2}} + 1) \quad (11)$$

$$g < h$$

$$g + h = n$$

Finally $I(s)_n$ is found by subtraction:

$$I(s)_n = I'_n - I(ns)_n = \sum (p'_g \cdot p'_h - p(ns)_g \cdot p(ns)_h) + \lambda \cdot \frac{1}{2} \cdot p(s)_{\frac{n}{2}} \cdot (p(s)_{\frac{n}{2}} + 2 \cdot p(ns)_{\frac{n}{2}} + 1) \quad (12)$$

$$g < h$$

$$g + h = n$$

The contents of the formulas given here correspond to the results obtained by Coffman¹¹. However, formula (10) can be even more simplified. From (9) it follows that

$$s'_{n-1} = 2 \cdot \sum T'_i \cdot T'_j + \lambda \cdot (T'_{\frac{n-2}{2}})^2 \quad \text{for } n > 2$$

$$i < j$$

$$i + j = n-2$$

Using (8a) we get:

$$s'_{n-1} = 2 \cdot \sum p'_g \cdot p'_h + \lambda \cdot (p'_{\frac{n}{2}})^2 \quad \text{for } n > 2$$

$$1 < g < h$$

$$g + h = n$$

or since

$$p'_1 \cdot p'_{n-1} = p'_{n-1}$$

we have

$$s'_{n-1} = -2 \cdot p'_{n-1} + 2 \cdot \sum p'_g \cdot p'_h + \lambda \cdot (p'_{\frac{n}{2}})^2 \quad \text{for } n > 2$$

$$g < h$$

$$g + h = n$$

which compared with (10) gives:

$$I'_n = p'_{n-1} + \frac{1}{2} \cdot s'_{n-1} + \lambda \cdot \frac{1}{2} \cdot p'_{\frac{n}{2}} \quad \text{for } n > 2 \quad (13)$$

This formula is valid for $n > 2$, but it is easily found that $I'_2 = 1$.

Formula (13) may also be derived as follows. In the isomeric alkynes C_nH_{2n-2} α) a terminal carbon atom takes part in the triple bond, or β) no terminal carbon atom takes part in the triple bond. Alkynes of type α may be

derived from the primary radicals R_{n-1} by removing two hydrogen atoms from the primary carbon atom, and thereafter attaching the resulting tervalent radical to $\equiv \text{C}-\text{H}$. By so doing no stereoisomerism is destroyed, and this procedure results in p'_{n-1} different alkynes. Alkynes of type β may be derived from the secondary radicals R_{n-1} (where $n > 2$) by removing the hydrogen atom and the radical R_a from $\begin{array}{c} R_a \\ \diagup \\ \text{C} \\ \diagdown \\ R_b \end{array} \begin{array}{c} \text{H} \\ \diagup \\ \diagdown \end{array}$, and thereafter attaching the resulting tervalent radical to $\equiv \text{C}-R_a$. By this procedure the number of asymmetric carbon atoms is reduced by one except in the cases where R_a is identical with R_b , and this occurs only when n is even, and in that case $a = b = \frac{n-2}{2}$. Identical groups will be attached to the secondary carbon atom of the radical R_{n-1} in $T'_{\frac{n-2}{2}} = p'_{\frac{n}{2}}$ number of cases. And therefore the number of alkynes belonging to type β must be:

$$\frac{1}{2} \cdot (s'_{n-1} - \lambda \cdot p'_{\frac{n}{2}}) + \lambda \cdot p'_{\frac{n}{2}} = \frac{1}{2} \cdot s'_{n-1} + \lambda \cdot \frac{1}{2} \cdot p'_{\frac{n}{2}}$$

Numerical values (quoted in the literature¹¹) of I'_n , $I(ns)_n$ and $I(s)_n$ for $n \leq 22$ are checked by means of (13) and (11).

C. *Alkenes*. This section will deal with the computation of 1) E'_n , 2) $E(ns)_n$ and 3) $E(s)_n$.

1) *The total number of stereoisomeric and non-stereoisomeric alkenes, E''* . A formula for computing E'_n can be derived by a method analogous to that which led to formula (6). We may think of an alkene as a hydrocarbon built up in the following way: From a primary or secondary radical R_g a hydrogen atom is removed from the primary or secondary carbon atom; and the same is done in the primary or secondary radical R_h . By joining the two resulting bivalent radicals in a double bond an alkene is produced. These bivalent radicals belong to one of the following two types:

a) The radicals in which two identical groups are attached to the carbon atom which takes part in the double bond,

β) the radicals in which two identical groups are not attached to the carbon atom which takes part in the double bond.

a) Let the radical of type α contain x carbon atoms.

For $x = 1$ there will be only one radical, namely $\text{H}_2\text{C}\diagdown$.

For x odd and > 1 there will be the radicals $(R_{\frac{x-1}{2}})_2\text{C}\diagdown$, where the two groups $R_{\frac{x-1}{2}}$ are identical. This makes a number equal to

$$T'_{\frac{x-1}{2}} = p'_{\frac{x+1}{2}}$$

For x even there will be no radicals of type α .

Finally we get that for all values of x there will be a number of radicals of type α equal to

$$\lambda \cdot p'_{\frac{x+1}{2}}$$

β) Let the radical of type β also contain x carbon atoms. The total number of bivalent radicals, containing x carbon atoms, of type α and type β is found equal to I'_{x+1} . This may be derived in the following manner. Every alkyne, $C_{x+1}H_{2x}$, is of the form $R_{x-1}-C\equiv C-H$ or $R_a-C\equiv C-R_b$, where $a+b=x-1$. If the triple bond in such an alkyne is broken off and the one carbon atom, contained in the triple bond, is removed, then from each such alkyne one radical may be derived, namely either $\begin{array}{c} R_{x-1} \backslash \\ H / \end{array} C \begin{array}{c} / \\ \backslash \end{array}$ or $\begin{array}{c} R_a \backslash \\ R_b / \end{array} C \begin{array}{c} / \\ \backslash \end{array}$. In this way no stereoisomerism is destroyed, and all possible bivalent radicals must appear.

For $x=1$ there will be no radicals of type β .

For $x>1$ there will be $(I'_{x+1} - \lambda \cdot p'_{\frac{x+1}{2}})$ radicals of type β .

However, using (13) we get:

$$\begin{aligned} I'_{x+1} - \lambda \cdot p'_{\frac{x+1}{2}} &= p'_x + \frac{1}{2} \cdot s'_x + \lambda \cdot \frac{1}{2} \cdot p'_{\frac{x+1}{2}} - \lambda \cdot p'_{\frac{x+1}{2}} \\ &= p'_x + \frac{1}{2} \cdot s'_x - \lambda \cdot \frac{1}{2} \cdot p'_{\frac{x+1}{2}} \end{aligned}$$

In the following considerations it is assumed that $n > 2$, and that each alkene may be considered as constructed of two bivalent radicals with respectively g and h carbon atoms, where $g \leq h$, and $g+h=n$.

For $g=1$ there will be 1 radical of type α and none of type β .

For $g>1$ there will be $\lambda \cdot p'_{\frac{g+1}{2}}$ radicals of type α and

$(p'_g + \frac{1}{2} \cdot s'_g - \lambda \cdot \frac{1}{2} \cdot p'_{\frac{g+1}{2}})$ radicals of type β or altogether

$(p'_g + \frac{1}{2} \cdot s'_g + \lambda \cdot \frac{1}{2} \cdot p'_{\frac{g+1}{2}})$ radicals.

For $h>1$ (and this is always the case as $n > 2$) there will be $\lambda \cdot p'_{\frac{h+1}{2}}$ radicals of type α and $(p'_h + \frac{1}{2} \cdot s'_h - \lambda \cdot \frac{1}{2} \cdot p'_{\frac{h+1}{2}})$ radicals of type β or a total of $(p'_h + \frac{1}{2} \cdot s'_h + \lambda \cdot \frac{1}{2} \cdot p'_{\frac{h+1}{2}})$ radicals.

When a radical of type α is joined in a double bond to a radical of type α or to a radical of type β no *cis-trans* isomerism is possible. On the other hand, if a radical of type β is joined to a radical of type β both a *cis* form and a *trans* form will occur.

Now the following can be found:

$$E'_n = p'_{n-1} + \frac{1}{2} \cdot s'_{n-1} + \lambda \cdot \frac{1}{2} \cdot p'_{\frac{n}{2}} \quad (\text{term I})$$

$$+ \sum_{\substack{1 < g < h \\ g+h=n}} (p'_g + \frac{1}{2} \cdot s'_g + \lambda \cdot \frac{1}{2} \cdot p'_{\frac{g+1}{2}}) \cdot (p'_h + \frac{1}{2} \cdot s'_h + \lambda \cdot \frac{1}{2} \cdot p'_{\frac{h+1}{2}}) \quad (\text{term II})$$

$$+ \sum_{\substack{1 < g < h \\ g+h=n}} (p'_g + \frac{1}{2} \cdot s'_g - \lambda \cdot \frac{1}{2} \cdot p'_{\frac{g+1}{2}}) \cdot (p'_h + \frac{1}{2} \cdot s'_h - \lambda \cdot \frac{1}{2} \cdot p'_{\frac{h+1}{2}}) \quad (\text{term III})$$

$$+ \lambda \cdot \frac{1}{2} \cdot (p'_{\frac{n}{2}} + \frac{1}{2} \cdot s'_{\frac{n}{2}} + \frac{1}{2} \cdot p'_{\frac{n+2}{4}}) \cdot (p'_{\frac{n}{2}} + \frac{1}{2} \cdot s'_{\frac{n}{2}} + \frac{1}{2} \cdot p'_{\frac{n+2}{4}} + 1) \quad (\text{term IV})$$

$$+ \lambda \cdot \frac{1}{2} \cdot (p'_{\frac{n}{2}} + \frac{1}{2} \cdot s'_{\frac{n}{2}} - \frac{1}{2} \cdot p'_{\frac{n+2}{4}}) \cdot (p'_{\frac{n}{2}} + \frac{1}{2} \cdot s'_{\frac{n}{2}} - \frac{1}{2} \cdot p'_{\frac{n+2}{4}} + 1) \quad (\text{term V})$$

Term I is due to $g = 1$ and $h = n-1$.

Term II is due to $1 < g < h$, when all alkenes are counted, those appearing in both *cis* form and *trans* form are, however, counted as one.

Term III is due to $1 < g < h$, when each alkene appearing in both *cis* form and *trans* form is counted as one again.

Term IV is due to $g = h = \frac{n}{2}$, when all alkenes are counted, those appearing in both *cis* form and *trans* form are, however, counted as one.

Term V is due to $g = h = \frac{n}{2}$, when each alkene appearing in both *cis* form and *trans* form is counted as one again.

By reduction we get:

$$E'_n = p'_{n-1} + \frac{1}{2} \cdot s'_{n-1} + \lambda \cdot \frac{1}{2} \cdot p'_{\frac{n}{2}} \quad (\text{term I})$$

$$+ 2 \cdot \sum_{\substack{1 < g < h \\ g+h=n}} (p'_g + \frac{1}{2} \cdot s'_g) \cdot (p'_h + \frac{1}{2} \cdot s'_h) + \lambda \cdot \frac{1}{2} \cdot \sum_{\substack{1 < g < h \\ g+h=n}} p'_{\frac{g+1}{2}} \cdot p'_{\frac{h+1}{2}} \quad (\text{term II} + \text{III})$$

$$+ \lambda \cdot (p'_{\frac{n}{2}} + \frac{1}{2} \cdot s'_{\frac{n}{2}}) \cdot (p'_{\frac{n}{2}} + \frac{1}{2} \cdot s'_{\frac{n}{2}} + 1) + \lambda \cdot \frac{1}{4} \cdot (p'_{\frac{n+2}{4}})^2 \quad (\text{term IV} + \text{V})$$

However, according to (9) the following must be true:

$$\lambda \cdot s'_{\frac{n}{2}} = \lambda \cdot 2 \cdot \sum_{\substack{a < b \\ a+b = \frac{n-2}{2}}} T'_a \cdot T'_b + \lambda \cdot (T'_{\frac{n-2}{4}})^2$$

and by introduction of (8a) this can be written as:

$$\lambda \cdot s'_{\frac{n}{2}} = \lambda \cdot 2 \cdot \sum_{\substack{1 < c < d \\ c+d = \frac{n+2}{2}}} p'_c \cdot p'_d + \lambda \cdot (p'_{\frac{n+2}{4}})^2$$

$$= \lambda \cdot 2 \cdot \sum_{\substack{1 < g < h \\ g + h = n}} p'_{\frac{g+1}{2}} \cdot p'_{\frac{h+1}{2}} + \lambda \cdot (p'_{\frac{n+2}{4}})^2$$

This expression for $s'_{\frac{n}{2}}$ is substituted in the above formula for E'_n :

$$\begin{aligned} E'_n &= p'_{n-1} + \frac{1}{2} \cdot s'_{n-1} + \lambda \cdot \frac{1}{2} \cdot p'_{\frac{n}{2}} + 2 \cdot \sum_{\substack{1 < g < h \\ g + h = n}} (p'_g + \frac{1}{2} s'_g) \cdot (p'_h + \frac{1}{2} s'_h) \\ &\quad + \lambda \cdot \frac{1}{4} \cdot s'_{\frac{n}{2}} + \lambda \cdot (p'_{\frac{n}{2}} + \frac{1}{2} \cdot s'_{\frac{n}{2}}) \cdot (p'_{\frac{n}{2}} + \frac{1}{2} \cdot s'_{\frac{n}{2}} + 1) \\ \text{or} \quad E'_n &= p'_{n-1} + \frac{1}{2} \cdot s'_{n-1} + 2 \cdot \sum_{\substack{1 < g < h \\ g + h = n}} (p'_g + \frac{1}{2} \cdot s'_g) \cdot (p'_h + \frac{1}{2} \cdot s'_h) \\ &\quad + \lambda \cdot (p'_{\frac{n}{2}} + \frac{1}{2} \cdot s'_{\frac{n}{2}}) \cdot (p'_{\frac{n}{2}} + \frac{1}{2} \cdot s'_{\frac{n}{2}} + \frac{3}{2}) \end{aligned} \quad (14)$$

This formula is valid for $n > 2$, but it is easily found that $E'_2 = 1$.

2) *The number of non-stereoisomeric alkenes, $E(ns)_n$.* The non-stereoisomeric alkenes must be derived from two non-stereoisomeric bivalent radicals, which are joined in a double bond in such a manner that no *cis-trans* isomerism is produced. These bivalent radicals belong to one of the following two types:

α) The radicals in which two identical groups are attached to the carbon atom which takes part in the double bond,

β) the radicals in which two identical groups are not attached to the carbon atom which takes part in the double bond.

α) Let the radicals of type α contain x carbon atoms.

For $x = 1$ there will be only one radical, namely $\text{H}_2\text{C}\langle$.

For x odd and > 1 there will be the radicals $(R_{\frac{x-1}{2}})_2\text{C}\langle$, where the two non-stereoisomeric groups $R_{\frac{x-1}{2}}$ are identical. This gives altogether

$$T(ns)_{\frac{x-1}{2}} = p(ns)_{\frac{x+1}{2}}$$

For x even there will be no radicals of type α .

Finally we get that for all values of x there will be a number of radicals of type α equal to

$$\lambda \cdot p(ns)_{\frac{x+1}{2}}$$

β) Let the radical of type β also contain x carbon atoms. The total number of bivalent radicals, containing x carbon atoms, of type α as well as type β , is equal to $I(ns)_{x+1}$. This is seen in the same way as above, where the number of stereoisomeric and non-stereoisomeric bivalent radicals was found.

The number of radicals of type β is consequently for all values of x equal to

$$I(ns)_{x+1} - \lambda \cdot p(ns)_{\frac{x+1}{2}}$$

In the following considerations it is assumed that each alkene may be considered as constructed of two bivalent radicals with respectively g and h carbon atoms, where $g + h = n$. To avoid *cis-trans* isomerism one of the radicals must be of type α , while the other may be either of type α or of type β .

Now the following can be found:

$$E(ns)_n = \lambda \cdot \sum_{\substack{g < h \\ g + h = n}} p(ns)_{\frac{g+1}{2}} \cdot I(ns)_{h+1} \quad (\text{term I})$$

$$+ \lambda \cdot \sum_{\substack{g < h \\ g + h = n}} (I(ns)_{g+1} - p(ns)_{\frac{g+1}{2}}) \cdot p(ns)_{\frac{h+1}{2}} \quad (\text{term II})$$

$$+ \lambda \cdot \frac{1}{2} \cdot p(ns)_{\frac{n+2}{4}} \cdot (p(ns)_{\frac{n+2}{4}} + 1) \quad (\text{term III})$$

$$+ \lambda \cdot p(ns)_{\frac{n+2}{4}} \cdot (I(ns)_{\frac{n+2}{2}} - p(ns)_{\frac{n+2}{4}}) \quad (\text{term IV})$$

Term I is due to $g < h$; the radicals of type α with g carbon atoms are here combined with the total number of radicals with h carbon atoms.

Term II is due to $g < h$; the radicals of type β with g carbon atoms are here combined with the radicals of type α with h carbon atoms.

Term III is due to $g = h = \frac{n}{2}$; the radicals of type α are here combined mutually.

Term IV is due to $g = h = \frac{n}{2}$; the radicals of type α are here combined with the radicals of type β .

By reduction we get:

$$\begin{aligned} E(ns)_n = & \lambda \cdot \sum_{\substack{g < h \\ g + h = n}} [p(ns)_{\frac{g+1}{2}} \cdot I(ns)_{h+1} + I(ns)_{g+1} \cdot p(ns)_{\frac{h+1}{2}}] + \lambda \cdot p(ns)_{\frac{n+2}{4}} \cdot I(ns)_{\frac{n+2}{2}} \\ & - \lambda \cdot \sum_{\substack{g < h \\ g + h = n}} p(ns)_{\frac{g+1}{2}} \cdot p(ns)_{\frac{h+1}{2}} - \lambda \cdot \frac{1}{2} \cdot (p(ns)_{\frac{n+2}{4}})^2 + \lambda \cdot \frac{1}{2} \cdot p(ns)_{\frac{n+2}{4}} \end{aligned}$$

However, according to (11) the following must be true:

$$\lambda \cdot I(ns)_{\frac{n+2}{2}} = \lambda \cdot \sum_{\substack{g < h \\ g+h=n}} p(ns)_{\frac{g+1}{2}} \cdot p(ns)_{\frac{h+1}{2}} + \lambda \cdot \frac{1}{2} \cdot (p(ns)_{\frac{n+2}{4}})^2 + \lambda \cdot \frac{1}{2} \cdot p(ns)_{\frac{n+2}{4}}$$

This expression is substituted in the above formula for $E(ns)_n$; we get:

$$E(ns)_n = \lambda \cdot \sum_{\substack{g < h \\ g+h=n}} p(ns)_{\frac{g+1}{2}} \cdot I(ns)_{\frac{h+1}{2}} - \lambda \cdot I(ns)_{\frac{n+2}{2}} + \lambda \cdot p(ns)_{\frac{n+2}{4}} \quad (15)$$

Note: The demand for $g < h$ is dropped in the first term above.

3) The number of stereoisomeric alkenes, $E(s)_n$. Finally $E(s)_n$ is found by subtraction:

$$E(s)_n = E'_n - E(ns)_n \quad (16)$$

Numerical values of E'_n , $E(ns)_n$ and $E(s)_n$ for $n \leq 22$ are calculated by means of the formulas (14), (15) and (16) (Table 2). The results have been checked by writing down all the formulas of the alkenes for $n \leq 10$.

Table 2. The number, E'_n , of stereoisomeric and non-stereoisomeric alkenes, the number, $E(ns)_n$, of non-stereoisomeric alkenes and the number, $E(s)_n$, of stereoisomeric alkenes with n carbon atoms ($1 < n \leq 22$).

| n | E'_n | $E(ns)_n$ | $E(s)_n$ |
|-----|-------------|-----------|-------------|
| 2 | 1 | 1 | 0 |
| 3 | 1 | 1 | 0 |
| 4 | 4 | 2 | 2 |
| 5 | 6 | 4 | 2 |
| 6 | 18 | 8 | 10 |
| 7 | 42 | 14 | 28 |
| 8 | 118 | 26 | 92 |
| 9 | 314 | 48 | 266 |
| 10 | 895 | 88 | 807 |
| 11 | 2 521 | 159 | 2 362 |
| 12 | 7 307 | 287 | 7 020 |
| 13 | 21 238 | 516 | 20 722 |
| 14 | 62 566 | 924 | 61 642 |
| 15 | 185 310 | 1 646 | 183 664 |
| 16 | 553 288 | 2 925 | 550 363 |
| 17 | 1 660 490 | 5 184 | 1 655 306 |
| 18 | 5 011 299 | 9 163 | 5 002 136 |
| 19 | 15 190 665 | 16 155 | 15 174 510 |
| 20 | 46 244 031 | 28 423 | 46 215 608 |
| 21 | 141 295 042 | 49 912 | 141 245 130 |
| 22 | 433 200 573 | 87 487 | 433 113 086 |

FINAL REMARKS

The calculations in this paper follow the line which has been pointed out by Henze and Blair. Calculations in connection with isomerism can also be discussed mathematically as shown by Polya¹². Also approximations, becoming more and more accurate the greater n becomes, can be set up¹³. Further calculations by extrapolation can be carried through^{4, 5}.

SUMMARY

Formulas for the number of isomeric alkynes and alkenes — with and without taking stereoisomerism into account — are derived.

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