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New Proof of the Number of Ways of Forming Noncyclic n-Mers

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New Proof of the Number of Ways of Forming Noncyclic n-Mers

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ABSTRACT

When every valency in n monomer units is assigned an individual index number, a unique formula can be written for each noncyclic n-mer by systematically listing the pairs of valencies forming the (n - 1) bonds. The chosen system allows the formulae to be partitioned into families and subfamilies and the number of ways of pairing the valencies in any set to be deduced. This leads to a new method of calculating the number of ways of forming noncyclic n-mers.

The solution to the problem of calculating the number of ways in which a noncyclic n-mer can be formed from n distinguishable, f-functional, monomer units with distinguishable valencies was published by Stockmayer [1] and again by Goldberg [2], who both made acknowledgment to Mayer and Mayer [3], where reference was also given to Harrison [4]. In the proof, monomer units were represented by mechanical frames containing f holes. A bond was formed by connecting two holes on different frames with a bolt. When an n-mer had been bolted together all unused holes were filled with a bolt. The n-mer was then dissociated into n separate frames each containing (f - 1) holes filled by bolts and one empty hole, with one free bolt left over. If the free bolt is chosen first, the empty hole in each of the n frames is thereby uniquely determined. The last sentence does not seem obvious and may require additional clarification by the reader. The ensuing proof is more general and appears to avoid this difficulty.

The number W is obtained by calculating the number of possible formulae for noncyclic n-mers. To obtain a unique formula for any n-mer it is necessary only to list the pairs of valencies forming the bonds according to an arbitrary system. A valency is denoted by ij, where i is the unit index and j its index on that unit. To make the proof general, the i-th unit has f_i valencies. All products and sums are taken from i = 1 to i = n.

In the system chosen here for writing formulae the used valency of the terminal unit of lowest index (TULI) is recorded and on its right-hand side (RHS) is put the valency on unit x to which it is joined; underneath, another used valency on unit x is written and the one coupled with it put on its RHS. When all used valencies on x have been recorded, the same process is adopted for the other units. Since each unit added to the first needs one bond, there are (n - 1) bonds.

The important point is that on the RHS must always appear a valency of a new unit. Since the top LHS valency and the (n - 1) RHS valencies all lie on different units, they must comprise a family set, and the formulae of all the possible noncyclic n-mers can be classified into equal families, a formula belonging to a particular family if the top LHS and all RHS valencies are those of its set. The number of families is the number of ways of choosing one valency from each unit, namely Πf_i.

Each family can be partitioned into equal subfamilies. For members of a given subfamily the remaining (n - 2) LHS valencies needed to complete the (n - 1) bonds are identical. Once the family set has been chosen (and on models the valencies could be labeled F, say) the subfamily set (labeled s) can be chosen from the other $(\Sigma f_i - n)$ valencies in ${}^{\Sigma f_i - n}C_{n-2}$ ways.

Once the subfamily set has been selected, the F-valency on the TULI is automatically defined and is put with it. It remains to determine only in how many ways these valencies can be paired with the other (n - 1) F-valencies. Since the order of bond formation is immaterial, the TULI valency is kept till the end to block the last F-valency on the (n - 1)-mer. Any s-valency has a choice of (n - 2) F-valencies [not (n - 1), because, as all s-valencies are on internal units, one F-valency must be on the same unit and is therefore forbidden]. As each bond formed restricts the choice by one, the second valency has a choice of (n - 3), the third (n - 4), and so on. When the last s-valency forms a bond there are two F-valencies left, but there is only one "choice" because one of the two lies on its own structure and is therefore forbidden. Hence there are (n - 2)! ways of forming the bonds in a subfamily.

Thus

$$W = {}^{\Sigma f_i - n}C_{n-2}\,(n-2)!\,\Pi f_i$$

$$= \frac{(\Sigma f_i - n)!\,\Pi f_i}{(\Sigma f_i - 2n + 2)!}$$

When all $f_i = f$, this reduces to $f^n(fn - n)!/(fn - 2n + 2)!$ as found previously [1, 2].

Two difficulties are anticipated. First, it might be thought that when an s-valency, xy, say, blocks an F-valency pq, a subsequent s-valency, say, pr, will not have had its choice restricted by 1 since pq was forbidden anyway. However units x and p are now joined, which means that the F-valency on unit x is forbidden to pr, so the choice is still reduced by one.

Second, if the arbitrary rule of placing the TULI valency on the LHS of the first bond is broken and that of another TU is put there, obviously the structure of the molecule is unaffected by its formula being written according to a different convention. The only result is that bonds in the pathway from the new TU to the old are written back to front; thus the same structure is assigned to a different family and subfamily which between them use identical valencies. The rule must therefore be kept to avoid repetition of structures.

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