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A Comment on Nomenclature and the Unsaturated Bond

D. J. POLTON*

Department of Computer Science, University of Hull, Hull HU6 7RX, England

The rules for naming compounds containing both double and triple bonds are unnecessarily complicated by the seniority given to the double bond over the triple bond. Although it is realized that the situation cannot be changed without great upheaval, it is hoped that by drawing attention to an anomalous situation which has been perpetrated throughout the world of chemical notation as well as nomenclature, any newly devised system will be a little better by avoiding it.

One of the curiosities of most, if not all, forms of chemical nomenclature and notation is the order of seniority allotted, for the purpose of enumeration, to the degree of unsaturation of carbon–carbon bonds. Double bonds are considered the most senior form of bond, although they are an intermediate form between the fully hydrogenated (single) bond and the fully unsaturated (triple) bond.
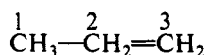
In reality, there should only be two possible orders of seniority of bonds, that of increasing or decreasing hydrogenation between the two atoms. Other orders, where the single or the triple bond comes between the others, do not seem to be logical. It could be said that the double bond is of more frequent occurrence than the triple bond and should therefore take precedence over it, but the bond by far most frequently seen in structures is single. And as for alphabetization, -en comes between -an and -yn.

It is therefore logical that if the double bond is considered to be senior to the triple bond then the single bond must be senior to the double bond. As in general nomenclature and notation, if the former is true then the single bond should be senior to the double bond.
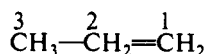
Consider the simplest case of propene:

$$CH_3—CH_2=CH_2$$

Taking the single bond to be senior, the enumeration should be

$$\overset{1}{C}H_3—\overset{2}{C}H_2=\overset{3}{C}H_2$$

But in IUPAC nomenclature[1] it is, of course

$$\overset{3}{C}H_3—\overset{2}{C}H_2=\overset{1}{C}H_2$$

*Present address: Rosefarm; Denne Manor Lane, Shottenden, Canterbury, Kent CT4 8JJ, England.

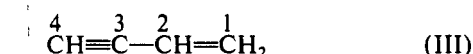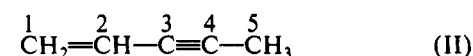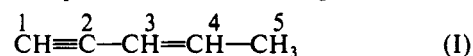That is, the double bond is senior to the single bond.

Therefore the triple bond should logically be senior to the double bond.

In IUPAC nomenclature the endings -ane, -ene, and -yne are given to compounds containing single bonds only, single and double bonds only, and triple with any other bond type, respectively. Structures with both double and triple bonds have the "en" in a position inferior to the "yne", as in -enyne or -adienyne. This implies that the most senior bond type is triple, as its ending overrides the presence of double bonds. Quite probably this order stems from alphabetization, -a, -e, -y, which is incidentally the order of increasing unsaturation.

Thus, although consideration of locants for a series of similar features before consideration of what those features are specifically is very important in any hierarchical scheme, the seniority given to the double bond for the purpose of enumeration does seem to be anomalous.

Further complication ensues on enumeration of a chain containing both double and triple bonds. IUPAC rule A-3.3 requires that the lower (at the first point of difference) numbering set be assigned to the positions of unsaturation, whether double or triple bonds. If both a double and a triple bond occupy the same position with respect to the ends of the chain, then the double bond is taken as prior. Single bonds are ignored.

The following examples of IUPAC numbering illustrate this:

$$\overset{1}{C}H\equiv\overset{2}{C}—\overset{3}{C}H=\overset{4}{C}H—\overset{5}{C}H_3 \qquad (I)$$

$$\overset{1}{C}H_2=\overset{2}{C}H—\overset{3}{C}\equiv\overset{4}{C}—\overset{5}{C}H_3 \qquad (II)$$

$$\overset{4}{C}H\equiv\overset{3}{C}—\overset{2}{C}H=\overset{1}{C}H_2 \qquad (III)$$

In I and II, 1,3 being lower than 2,4, the prior consideration is that terminal bond having the highest degree of unsaturation.

In III it is that terminal bond having the lowest degree of unsaturation.

Thus in I, the terminal triple bond has become the dominating factor in establishing the order of carbons in the chain.

When it comes to naming the structures in full, alphabetization of endings must take effect. The IUPAC names of the above are (putting the 1's in)

I   3-penten-1-yne or pent-3-en-1-yne
II   1-penten-3-yne or pent-1-en-3-yne
III   1-buten-3-yne or but-1-en-3-yne

The double bond being senior to the triple bond in IUPAC nomenclature, structure I ought to be named 2-penten-4-yne. Rule A.3-3 has overriden this.

If the logical order of increasing seniority were taken solely as that of increasing unsaturation, single-double-triple, and this were adhered to in all cases of mixed degrees of unsaturation, i.e., if there were a single strict rule for the enumeration of unsaturated structures, the above anomalies would disappear; not only would the naming of these structures be simpler, but computer processing of nomenclature would be less complicated.[2] But as far as has been ascertained, the IUPAC ruling on the seniority of the double bond has been adopted in other major forms of nomenclature and notation which use a numbering system for chains.[3-6] Only in the author's own development of the Dyson–IUPAC notation, in use from 1965 to 1981, was the strict order suggested incorporated.[7]

Using this suggested order of seniority, IUPAC names for I to III would become

I   3-penten-1-yne or pent-3-en-1-yne
II   4-penten-2-yne or pent-4-en-2-yne
III   3-buten-1-yne or but-3-en-1-yne

It may be argued that for the purposes of nomenclature the single bond does not have to be considered at all, and therefore it does not matter in which order double and triple bonds are placed. An analogy may be that with all organic structures carbon is considered only after everything else. But in stereoisomerism single bonds have to be considered and are considered last.

CONCLUSION

It is of course not possible to change long-established rules of nomenclature on which many thousands of compounds have been named in the scientific literature. But the purpose of this comment is to point out a seemingly anomalous situation, which it is hoped will not be propagated into any new form of chemical nomenclature or notation which might be suggested for adoption as an alternative, or even eventually a replacement, of present-day IUPAC nomenclature.

ACKNOWLEDGMENT

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On the Determinant of the Adjacency-Plus-Distance Matrix as the Topological Index for Characterizing Alkanes

JAN V. KNOP, WOLFGANG R. MÜLLER, and KLAUS SZYMANSKI

Computer Centre, The Heinrich Heine University, 4000 Düsseldorf, Federal Republic of Germany

NENAD TRINAJSTIĆ*

The Rugjer Bošković Institute, P.O. Box 1016, 41001 Zagreb, The Republic of Croatia

The determinant of the adjacency-plus-distance matrix has been systematically tested for examples that would disprove a supposition that it is a unique topological index (TI) for alkanes. The analysis was carried out for alkane trees with up to 20 sites. The search was fruitful: The first pair of alkane trees with identical TI numbers was already found in the nonane family.

Schultz and co-workers[1] have recently introduced in this journal a novel topological (graph-theoretical) index (TI) for numerical characterization of alkanes. This index was defined as the determinant of the adjacency-plus-distance matrix

$$TI = \det|A + D|$$

where **A** is the adjacency ($N \times N$) matrix and **D** is the distance ($N \times N$) matrix.

The adjacency-plus-distance matrix **A** + **D** may be directly constructed for the labeled alkane tree. One has simply to input into the distance matrix of an alkane tree the digit 2 in all places where the distance of unity would be otherwise placed.

The authors[1] stated that this index "appears to be useful as a unique molecular topological index for each different alkane". Since the TI is a graph-theoretical descriptor with structural significance, the above statement needs verification. In this paper we will try to answer the important questions "Are the TI numbers unique?", and, if the answer is negative, "What are the smallest alkane trees for which TI is not unique?".

Since we are in the position to generate routinely all alkane trees up to a given number of sites[2] and have ready a computer program for construction of their distance matrices[3] and consequently for their adjacency-plus-distance matrices, we computed the TI numbers for all alkanes with up to 20 atoms