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"Carbomers". I. A General Concept of Expanded Molecules.

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Abstract. Carbo^n–molecules are defined by the insertion of n C_2 units into each bond of given molecules. Examples are suggested, the challenge of their synthesis being motivated by possible applications in fundamental organic chemistry, coordination chemistry and material science.

Molecular structures can be described as a combination of three consecutive features:[1] (i) *symmetry*, (ii) *size* and (iii) *energy* . Energy of molecular states can be changed more or less independently of size and symmetry by considering chemical analogs, i.e. by changing one element for another from the same column of the periodic table (Li→Na, Fe→Ru, C→Si, O→S, etc...). A logical progression is to seek a chemical variation for changing the size of a molecular structure without changing its symmetry. An expansion can affect the bond lengths but evidently not the size of real atoms: while the resulting energy change affects the contribution of interatomic van der Waals contacts in the total steric energy, within the limits of bond energy additivity, the sum of the other terms (not including resonnance energy) is anticipated to be preserved upon such a modification. A simple conceptual method for this process is proposed and discussed here.

The symmetry of a molecule is assumed to be largely unaltered by inserting one –C≡C– unit into *each* single bond A–B of the molecule. Indeed, the symmetry of the A–C≡C–B unit is the same as the local symmetry of the A–B unit. At the same time, one =C=C= unit must be inserted into each double bond A=B (the right angle between adjacent π orbitals in an allene unit guarantees that the planar substitution pattern of an olefin is retained in the expanded olefin). Finally, one ≡C–C≡ unit must be inserted into each triple bond A≡B. Bonds with higher orders (occuring between transition metal atoms[2]) cannot be elongated by this method, but they are very scarce, and are not encountered in organic chemistry. The expansion is not strictly homogeneous. However, each bonding distance AB is roughly augmented by a length $4r \approx 2.6$ Å in AC_2B, where r is an average covalent radius for *sp*-carbon atoms.[3] Evidently, greater expansions can be performed by inserting $n \geq 2$ C_2 units in each bond. Since the resulting structures mostly retain both the symmetry and the electronic relationships between original atoms (general vinylogy effect), and since they differ only by the number of carbon atoms (and thus by size), these structures are termed as "carbomers" of the original molecule, or, more precisely, as corresponding "carbo^n–molecules" (Fig. 1). For the sake of brevity, a "carbo^1–molecule" will be simply called a "carbo-molecule".[4] It is remarkable that carbon is the only element which is likely to be generally useable in such an expansion process.

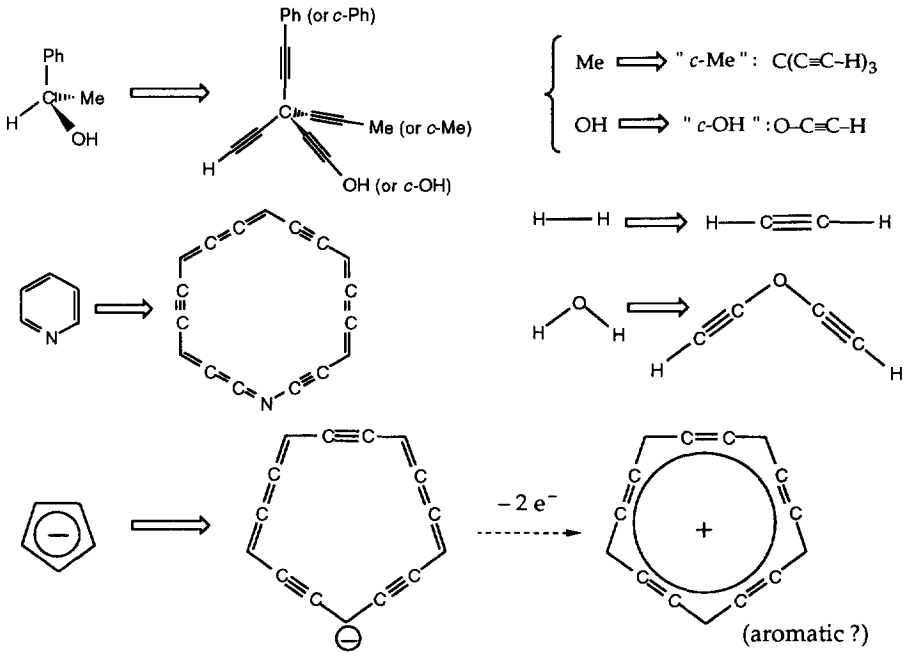

Figure 1. Examples of carbomers.

The expansion can be restricted to only one (or more) orbit of atom sites in the molecular skeleton.[5] For instance, the benzene molecule has two skeletal orbits: that constituted by the six carbon sites and that constituted by the six hydrogen sites. $[C,H]_6$carbo-benzene **1c** and $[C,H]_6$carbo^2-benzene have been already prepared.[6] The D_{6h} symmetry might be preserved in either of carbo-benzenes **1a** or **1b**: then, the "butatriene edges" and the "butyne edges" would be identical (Fig. 2).

As well as molecular skeletons which are defined by all the participating atoms, sub-skeletons are often considered for non-rigid molecules, where atom sets are gathered in groups: considering these groups as pseudoatoms, the subskeleton is defined by group sites instead of atom sites. The expansion can affect only the distances between groups but not between all constituting atoms. For example, expansion of a C–Me unit can be partially realized as C–C≡C–Me, whereas complete expansion of C–CH_3 gives C–C≡C–C(C≡C–H)$_3$.

It must be stressed here, that several related, but less systematic, processes of molecular expansion have been devised in order to separate functionalities (e.g. donor-acceptor ends of molecules with non-linear optical properties) by molecular fragments made of conjugated acetylene and arylacetylene units,[7] cubylacetylene units,[8] or simply conjugated alkene units (e.g. expanded porphyrins[9]). In a closely related process, "nacked" C_n units have been used to link like or unlike organometallic building blocks.[10]

Many compounds containing $(R–C≡C)_nX$ units (n=4 or 3, X=C,[11] Si,[12] Ge,[13] Pb,[14] Al,[15]...) have been prepared,[16] and it is entirely possible that some of the putative carbomers depicted in Fig. 1 and 2. would be unstable: attempts at synthesis or calculations will be necessary to demonstrate their stability or lack thereof. Beyond molecules, the concept can also be applied to materials: carbomers of covalent crystals (diamond or graphite,...) might have interesting properties (density, hardness, eletrical conductivity,...).

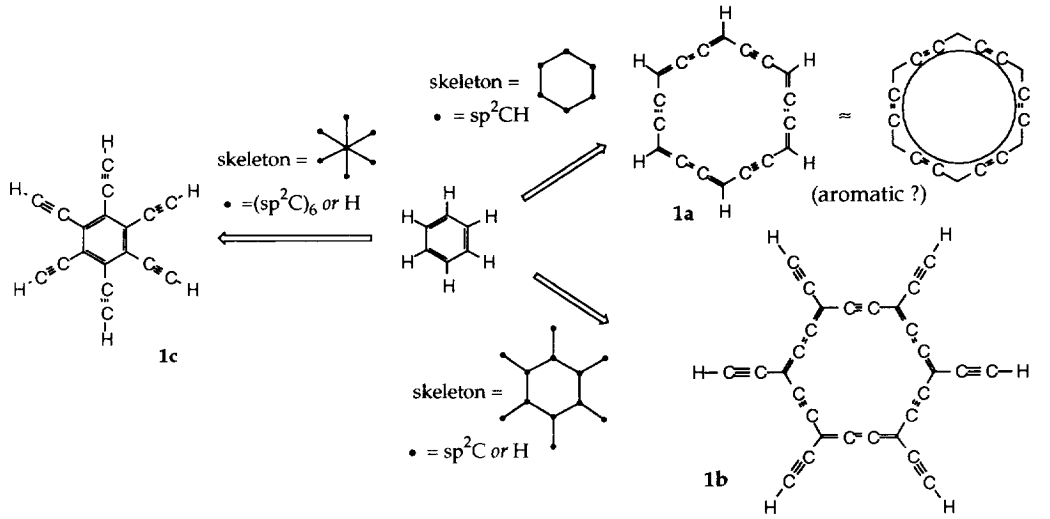

Figure 2. Expansion processes of the benzene molecule.

Coordination chemistry of ligand carbomers (carbo-benzene, carbo-cyclopentadienyl ions, etc.) might lead to novel modes of complexation: the electron ring (with a van der Waals thickness of *c.a.* 1.5 Å) should be large enough to "surround" large low-valent metal atoms such as lanthanides and actinides. The large ring size of carbo-benzene (7-8Å) suggests the possibility of aromatic catenanes (Fig. 3). The ring size of carbo^2-aromatics renders possible the drawing of macromolecular chains of interlocking rings which could be aromatic.[17] In the same vein, the polymerization of carbo-monomers merits study. Comparison of the rotatory power of chiral molecules with that of their carbomers should be interesting.[18] Finally, the systematic comparison of some reaction (e.g. $R_1R_2C{=}O{+}RLi$) with the corresponding reaction of carbomer reactants ($R'_1R'_2C{=}C{=}C{=}O{+}R'Li$, $R_i'{=}(c\text{-}R_i)\text{-}C{\equiv}C$) could be analyzed in terms of general "vinylogy effect".[19]

This list of potential applications for carbomers is not exhaustive but should encourage efforts for their synthesis. In particular, the preparation of carbo-benzenes deserves to be undertaken.[20]

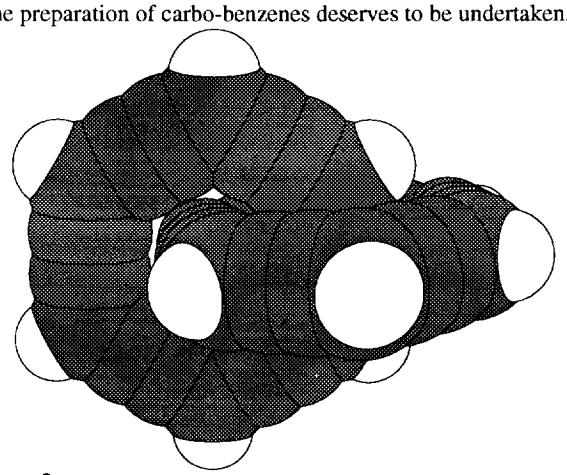

Figure 3. Space-filling view of interlocked $[C,C]_6$carbo-benzene molecules.

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References and Notes

1). The description of molecules requires a fourth feature, (iv) entropy (thermal population of conformations and molecular states), which can be independently and continuously modified by varying temperature.

2). See, for example: Stoner, T.C.; Greib, S.J.; Hopkins, M.D., *Angew. Chem. Int. Ed. Engl.*, **1993**, *32*, 409-410.

3). The relative expansion $\lambda = (d(A\text{-}B)+4r)/d(A\text{-}B)$ is constant only over a given skeletal orbit of bonds, wherein the initial bonding distances AB are about the same by definition (for a C_1 skeleton, the expansion is "additive" rather than "multiplicative": non-bonding interatomic distances are not expanded in the same way). Nevertheless, the expansion of a N-bond molecule results in a 3N-bond structure: considering that all bond lengths are of the same order of magnitude ($\approx$1.5$\pm$0.5 Å), the expansion could be regarded as a homothet of factor $\lambda \approx 3$.

4). The "carbo^0-molecule" corresponds to the non-expanded carbomer.

5). If all the bonds of a molecule undergo the insertion of n C_2 units, the resulting structure can be precisely termed as the corresponding "*per*carbo^n-molecule". If only m bonds i_1–j_1,..., i_m–j_m undergo this insertion, then the structure can be termed as the corresponding [i_1–j_1]...[i_m–j_m]-carbo^n–molecule. It must be emphasized that in order to preserve the original symmetry and thus obtain a *carbomer*, all the bonds of a given skeletal orbit must undergo the same expansion.

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19). If the ynoxide adduct $R'R'_1R'_2C\text{–}C{\equiv}C\text{–}O\text{–}Li$ is quenched with water, the resulting ynol is unstable (Wagner, B.D.; Zgierski, M.Z.; Lusztyk, J., *J. Am. Chem. Soc.* **1994**, *116*, 6433-6434) and tautomerizes to the ketene $R'R'_1R'_2C\text{–}CH{=}C{=}O$, which does not correspond to the geometrical expansion of the "normal" alcool $RR_1R_2C\text{–}OH$ (even if OH is considered as one ligand on a subskeleton where the O–H bond does not appear). But if the ynoxide adduct (which is not the *per*carbo-adduct, for the O–Li bond is not expanded) is formally quenched with diethynylether (Fig. 2), the carbomer product $R'R'_1R'_2C\text{–}C{\equiv}C\text{–}O\text{–}C{\equiv}C\text{–}H$ might be obtained.

20). Chauvin, R., accompanying paper in this Journal.

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