Technical comment on "sp-hybridized molecular carbon allotrope, cyclo[18]carbon

J. F. Ogilvie, scientist and professor,
Simon Fraser University Canada and Universidad de Costa Rica

(25 September 2019)

J. F. Ogilvie, Centre for Experimental and Constructive Mathematics, Department of Mathematics, Simon Fraser University, Burnaby, British Columbia V5A 1S6 Canada and Escuela de Quimica, Universidad de Costa Rica, San Pedro de Montes de Oca, San Jose, Costa Rica

abstract The attribution of sp-hybridization to cyclo[18]carbon lacks scientific validity.

As a result of his extensive quantitative research investigations, the late eminent structural chemist Professor Lawrence Bartell declared [1], more than two decades ago, "Hybridization is a fraud!", but this documented fraud [2,3] continues to reap its unwitting victims. As an instance of this fraud, a recent article [4] bears the condemnable title "An sp-hybridized molecular carbon allotrope, cyclo[18]carbon" and reports 'a polyynic structure with defined positions of alternating triple and single bonds". There is no discussion of the basis of that "sp-hybridized" structure other than an allusion to "sp-hybridized carbon allotropes is that they possess two perpendicular π-conjugated electron systems".
In 1931 Pauling [5] introduced such sp or digonal hybrid atomic orbitals, apparently as a linear combination of 2s and 2p orbitals of a hydrogen atom, although that origin was never explicitly stated. A direct application of such hybrid orbitals to explain molecular structure, rather than to use such functions in a basis set for calculations -- which is unobjectionable, has never been objectively justified [2,3]. Other than various unwarranted assumptions and inaccurate claims, such as that the radial dependence of 2s and 2p orbitals would be taken into account -- but was never so taken, Pauling [5] failed to disclose that alternative orbitals had been derived by Schroedinger in his third seminal paper [6] in 1926, which Pauling cited for other reasons in his monograph with Wilson [7].

The fact is that real, i.e. not complex, algebraic functions arise directly and naturally in the solution of the Schroedinger equation for the hydrogen atom in paraboloidal coordinates [6] that have exactly the same geometric shape and orientational features [8] as the functions that are constructed as those linear combinations of 2s and 2p functions in spherical polar coordinates. To be unremittingly explicit, when depicted in either case in cartesian coordinates -- which is the standard convention, a digonal hybrid orbital generated as a linear combination of 2s and 2p algebraic functions for the hydrogen atom in spherical polar coordinates has, according to a common criterion, exactly the same size, shape and orientation as an algebraic function for quantum numbers n1=1 and n2=m=0, or n2=1 and n1=m=0, that results from a direct solution of the Schroedinger equation in paraboloidal coordinates. (Those solutions of the Schroedinger equation in spherical polar coordinates are formally applicable only for a one-electron atom in a rigorously spherical environment -- no other atoms in the vicinity, no electric field.) There is absolutely no necessity to introduce those digonal hybrid orbitals to describe the binding in a linear geometry. The deviation from linearity of any three adjacent atomic centres in the C18 ring in cyclo-C18 is significant; even smaller deviations from angles according to hybridization schemes were the basis of Bartell's denunciation [1], mentioned above.

These anomalies -- the deviation from the linearity formally required for sp hybridization and the ignorance of the existence of paraboloidal orbitals -- make the claim of "sp-hybridized carbon allotropes" [4] not only meaningless but even ludicrous. The claimed planar cyclic C18 molecule might well be an experimental artefact of the adsorbed state of these C18 species rather than being observed as a free molecule; the deviation from linearity of three adjacent atomic centres would be much larger if the free C18 molecule were not planar.

The production [4] of cyclo-C18, even in an adsorbed condition, is in any case a novel achievement; any sham embellishment of an account of that synthesis through invocation of sp-hybridization is an unnecessary distraction from scientific objectivity.

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