Design of neutral hydrocarbons having a planar tetracoordinate carbon

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Cyclopropyne (C₃H₂) and related spiro bicyclic structures show unusual structural preference for the planar tetracoordinate structure over the conventional tetrahedral arrangement. C₅H₄ has been proposed as the smallest neutral hydrocarbon with planar tetracoordinate carbon. NICS values indicate substantial stabilization of the planar arrangements over the tetrahedral counterparts.

The recognition of the preference of tetrahedral form for tetracoordinate carbon atoms by van't Hoff and Le Bel provided the basis for structural organic chemistry and laid foundations for the third dimension in chemical structures and bonding. Nearly about a century later, Hoffmann's group using the orbital symmetry principles critically analyzed the causative factors for the stability of the tetrahedral arrangement for a tetracoordinated carbon. Importantly, they put forth strategies to stabilize the planar tetracoordinate carbon (ptC). Over the past three decades or so, a number of elegant computational and experimental strategies towards stabilizing the planar tetracoordinate carbon (ptC) have been put forward. Two different approaches can be adopted to achieve to stabilize the ptC: the first one is to force the central carbon atom to be planar by structural constraints and the next is by electronic stabilization.

Stanton et al. have reported that the planar form of 1 (Fig. 1) is about 7 kcal/mol more stable than the tetrahedral form. While such unusual structural preference is exciting from theoretical point of view, it failed to enthuse the chemistry community since the planar structure, as well as the tetrahedral structure, is not a minima on the potential energy surface. In the present communication we venture to design, through structural, modifications so as to obtain a viable structure with planar tetracoordinate carbon (Fig. 1). Hybrid density functional theory B3LYP calculations with 6-31G* basis set were employed using the Gaussian 98 program package.

The relative energies of the planar and tetrahedral forms, and the number of imaginary frequencies obtained at the B3LYP/6-31G* level are given in Fig. 1. Encouragingly, in all the ten cases, the planar forms are more stable than the corresponding tetrahedral counterparts. While most structures are not minima on the potential energy surface, structure 3P is a minimum. To our knowledge, this is the smallest pure neutral hydrocarbon skeleton containing ptC, which is characterized as a minimum on the potential energy surface. The energy difference between the planar and tetrahedral forms of 3 is computed to be higher than that found in case of 1. We have examined the shapes of the frontier molecular orbitals to understand the unusual stability(Fig.2). Clearly, the unusual stability of the planar arrangement is traced to the unique bonding mode exhibited by the C₃-unit, with a highly delocalized π-framework which is the case in all the structures considered. The planar molecules exhibit substantial HOMO-LUMO energy gap compared to the tetrahedral ones indicating higher stability of the planar molecules except in 4⁺. Similarly, the aromatic stabilization in this class of compounds is demonstrated using the nucleus independent chemical shift (NICS) values. NICS criterion has become very useful to gauge the aromatic stabilization of conjugated systems in recent years. All the planar forms have high negative NICS values indicating aromaticity, whereas the tetrahedral forms possess nonaromatic/antiaromatic character.

In summary, the present study reports a novel class of ptC containing neutral hydrocarbons. All the spiro compounds considered here exhibit higher stability for the planar structural arrangement compared to the traditional tetrahedral forms. The planar form of 3 is computed to be a minimum on the potential energy surface and is more stable than the tetrahedral structure by about 74 kJ/mol. To our knowledge, this is the smallest neutral hydrocarbon skeleton proposed so far...
Fig. 1 – The relative energies (kJ/mol), number of imaginary frequencies (in parentheses), NICS values in ppm (bold face) and HOMO-LUMO energy gap in eV (italicized) obtained at the B3LYP/6-31G* level.
in the literature. The high stability for the planar form is traced to the delocalization in the C₃-ring, which is demonstrated using the shapes of molecular orbitals, NICS and HOMO-LUMO energy gap.

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References


Fig. 2- The isosurfaces (obtained using MOLDEN package) of the occupied molecular orbitals corresponding to bonding (a) and antibonding (b) combinations of the lone pairs on the two acetylenic carbons, π-bonding (c) and the valence bond structure proposed (d) for the C₃-unit. The pattern is qualitatively identical in all the structures considered.