

Bond Lengths in a Carbocation Explained in terms of Covalent Radius, Ground State Bohr Radius and the Golden Ratio

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Abstract The author has shown previously that the Golden ratio based ionic radii explain quantitatively the bond lengths in completely ionic as well as partially ionic bonds including hydrogen bonds. These ionic radii and covalent radii were shown to be additive in small as well as large molecules. This work shows that the published bond length data for a carbocation can also be explained using the covalent and Bohr radii and the Golden section of the ground state Bohr radius of carbon.

1. Introduction

The Golden sections [1,2] of covalent bond lengths $d(AA)$ between two atoms (A) of the same kind as the cationic and anionic radii, R_{A+} and R_{A-} respectively, can also be considered as the radii of the ionic forms in Pauling's [3] resonance structures of AA. These Golden ratio ($\phi = (5^{1/2}+1)/2$) based radii are given by (see [1,2] for all the details),

$$d(AA) = 2R_{A,\text{cov}} = R_{A+} + R_{A-} \quad (1)$$

$$R_{A+} = d(AA)/\phi^2, R_{A-} = d(AA)/\phi \quad (2a,b)$$

where $R_{A,\text{cov}}$ is the covalent radius of A.

The best proof of the validity of the above relations was demonstrated [1] for the alkali halides: the Golden ratio based cationic and anionic radii of alkali metals and halogens respectively, exactly add up to give the crystal ionic distances in alkali halides [1], without any need for Pauling's [3] empirical 'radius ratio corrections'. Similarly, partial ionic bonds as in hydrogen halides and metal hydrides were shown to be exact sums of the covalent radii of one atom and the Golden ratio based ionic radius of the other [1,2]. The latter also showed that covalent and ionic radii are additive. The Golden sections of the ground state Bohr radii obtained from the first ionization potentials were shown to be related to the covalent and other types of atomic radii for the elements of the Periodic Table. Also could be explained the bond lengths and bond angles of some molecules and molecular ions. The results obtained over many years for small as well as large inorganic, organic and biological molecules can be found in the collected papers in [4].

2. Present work

In this work, the author shows for the first time that that the Golden ratio also plays a role in explaining the bond lengths in a carbocation, described in the epoch making paper by Olah et al [5]. The bond lengths in a simple carbocation shown in Fig. 9 C₂ in [5] were chosen for the study here. This diagram is presented here as Fig. 1.

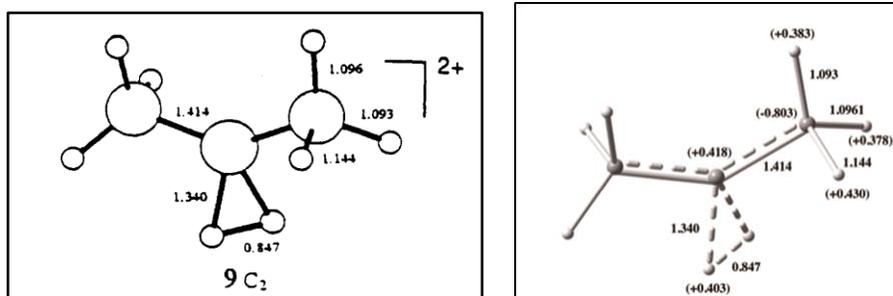
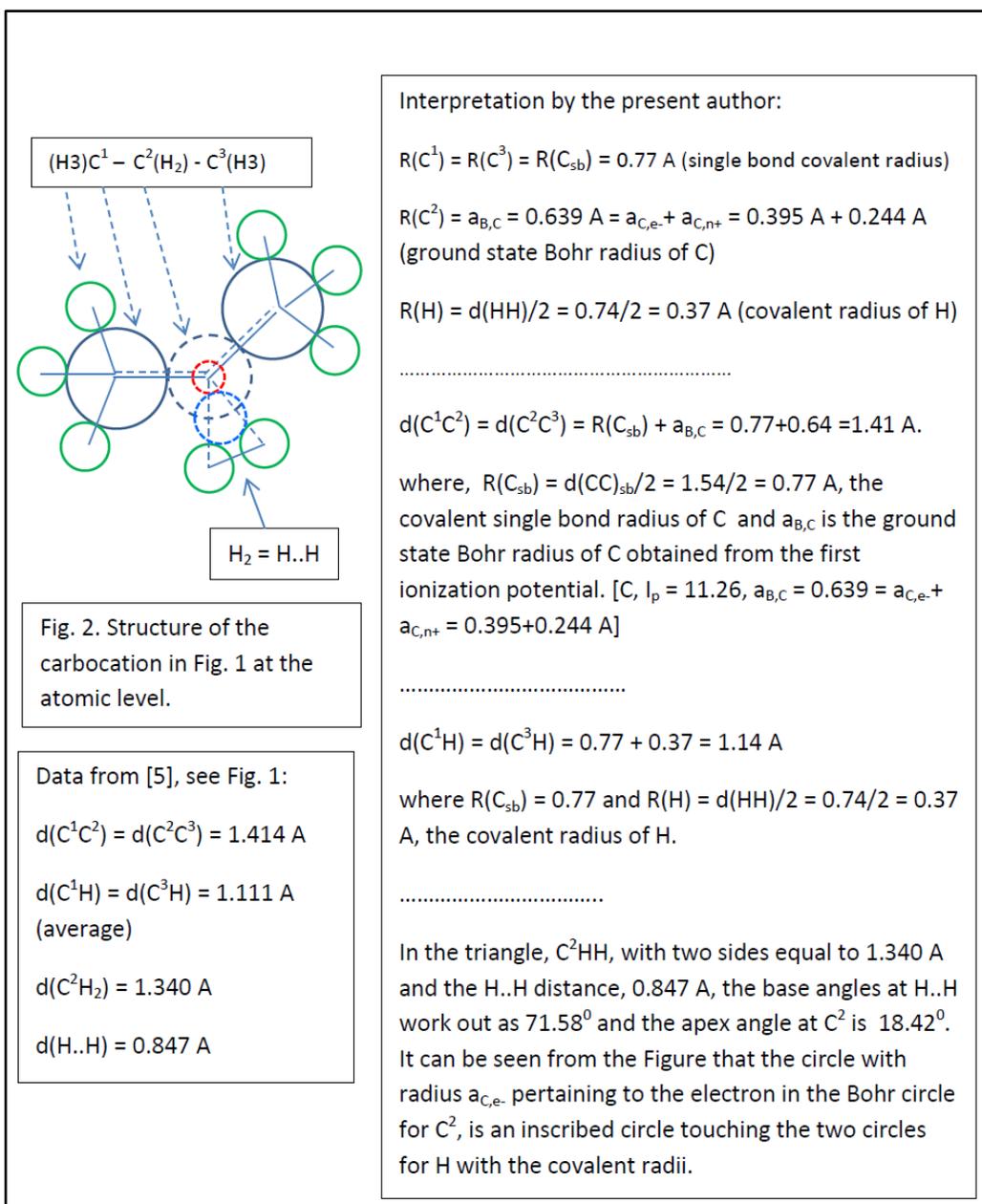


Fig. 1. The diagram on the left is Fig. 9C₂, β- protonated 2-propyl cation 9 (C₂ symmetry), H(3)C-C(H₂)-CH(3) cation from [5] and the one on the right was kindly provided by one of the authors, Prakash in [5].

The bond length data in the above carbocation (see Fig. 1) are interpreted by the author in terms of the single bond covalent radius $R(C_{sb})$ for the two methyl carbons, C¹ and C³ and the ground state Bohr radius, $a_{B,C}$ for the central carbon, C², (see Fig. 2). The Bohr radius, derived from the first ionization potential, is also divided into the Golden sections, a_{B+} and a_{e-} pertaining to the positive nucleus and the outer electron.

In Fig. 2, all the hydrogens marked by green circles have the covalent radii, $R(H) = d(HH)/2$, where $d(HH)$ is the interatomic distance in molecular hydrogen. The various radii of carbon and its Bohr radius are related to each other as described earlier [6]. The author's interpretation of the various bond lengths are provided in the column on the right side next to the Fig. 2.

It can be seen from the data and correlations in Fig. 2 that all bond lengths are accounted for by the additivity of radii of adjacent atoms and or ions.



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