Extraordinarily Long 2-Electron - 4-Center (2e⁻/4c) 2.9-Å Carbon-Carbon Bonds - What is a Chemical Bond?

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Carbon-carbon (CC) bonding is a key essence of organic and biochemistry. The length of a CC bond, *i.e.* 1.54 Å found in the diamond allotrope of carbon and ethane, is among the essential information learned by all chemistry students. This is the length of a single bond (σ) between sp³-hybridized carbons and is the longest of all common CC bonds. Our studies of the $[TCNE]_2^2$ (TCNE = tetracyanoethylene) dimers reveal that 2.89 ± 0.05 Å 2 electron/4 center (2e³/4c) CC bonds are present. Structural, spectroscopic, magnetic, and computational data supporting this multicenter formulation will be presented. These unusual bonds lead to unusual physical properties that will be discussed, as will what is a chemical bond? Furthermore, examples of long, multicenter C-C bonds existing for other dianions, *e.g.*, [cyanil]₂²-, as well as dications, *e.g.*, $[TTF]_2^{2+}$ (TTF = tetrathiafulvalene), and homo-, *e.g.*, [tri-t-butylphenalenyl]₂, and zwitterionic heterodimers *e.g.*, $TTF^{\delta+}_{\bullet,\bullet,\bullet}$ TCNE $^{\delta}$ ($\delta \sim 0.5$), will be discussed.