

Pancake bonds: π -Stacked dimers of organic and light-atom radicals



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ABSTRACT

The nature of the chemical bond is fundamental to the modern concept of chemistry. Species that exhibit unusual interactions provide a valuable challenge to current theoretical models and computational techniques. One of the areas that has garnered significant interest in the past decade is the computational analysis of so-called “pancake bonds” between planar organic or light-atoms radicals. The present review provides a timely survey of the more common organic and light-atom neutral radicals, radical cations and radical anions that are known to form π -dimers in the solid state.

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1. Introduction

The concept of chemical bonding is the foundation of modern chemistry. The bonding model traditionally taught in the college classroom invokes an electron pair and classifies bonds as either covalent or ionic, or some combination of these characters. Ionic bonding arises primarily from a Coulombic interaction between ions of opposite charge. By contrast, a covalent bond is one in which an electron pair is “shared” and the bond energy arises from the spin-pairing of the bonding electrons [1].

More complex bonding models have been developed in order to provide an explanation for unusual observations or phenomena. For example, Hiberty et al. proposed the “Charge-Shift” model wherein the bonding is primarily a function of extremely large covalent-ionic resonance energies [2,3]. The Charge-Shift model is particularly good at describing homonuclear bonding between very electronegative atoms (e.g., F–F, HO–OH) as well as heteronuclear bonding involving these atoms (e.g., H₃C–F). Negligible electron density between bonded O–O or N–N atoms in a number of species, as observed by X-ray diffraction [4] is correctly anticipated by the Charge-Shift model.

Molecular structures that are apparently difficult to describe using a simple covalent/ionic electron pair have likewise played an important role in the early development of bonding models. Pauling explicitly deals with 1-electron and 3-electron bonding in the abridged, “student version” [1] of his famous book *The Nature of the Chemical Bond*. Such 1- or 3-electron bonds between

two centers (atoms) have about half the bond strength of a traditional 2-electron bond. Examples of molecules to which this model can be applied include H₂⁺, He₂⁺ and NO. Pauling points out that aromatic or resonance stabilized species, such as benzene, can also be considered as possessing this type of “fractional bonding”.

The concept of multi-centered/2-electron (mc/2e) bonding is related to Pauling’s fractional bonding model. Although the idea invokes delocalization of the bonding electron pair, it is still a description of localized bonds and thus an extension of valence bond theory. Application of the mc/2e bonding model to organic compounds is generally restricted to unusual molecular species. The 3-centered/2-electron (3c/2e) bonding model has been used to describe the bonding in hypercoordinated carbon atoms [5] (i.e., carbon atoms that are nominally bonded to more than four atoms) such as various types of carbocations, including the methonium cation (CH₅⁺) [6,7] and the 1,6-dimethylcyclodecyl cation (Me₂C₁₂H₁₇⁺) [8]. The latter example involves a bridging hydrogen atom, nominally a C–H–C bond (Fig. 1) [9]. Organic compounds containing bridging hydrides are considered to be rather exotic, however bridging hydrides are not unusual in either main group inorganic or transition metal complexes [5,10,11]. Borohydrides, such as the triborohydride anion (B₃H₈[−]) [12], commonly include one or more B–H–B bonds, and a search of the Cambridge Structural Database [13] (CSD) reveals more than five thousand reported crystal structures of transition metal complexes with bridging M–H–M hydrides! Metal-bridging carbon atoms, M–C–M, are also quite common, identified in familiar species such as Al₂Me₆ [14] and Co₂(CO)₈ [15].

Multi-centered/multi-electron (mc/me) valence bond models [16] have been proposed to describe the bonding in S₂Cl₄²⁺ (and

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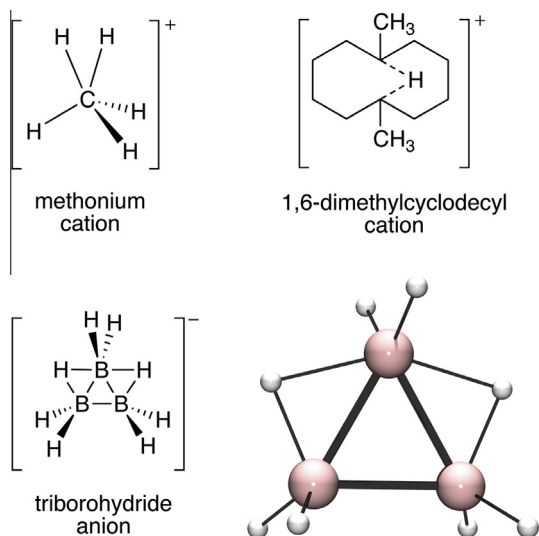


Fig. 1. (Top) Line drawings of species containing hypercoordinated carbon atoms. (Bottom) Line drawing and image of the solid state structure of $B_3H_8^-$ created from the crystallographic information file (CIF) of $[(NH_3)_2BH_2][B_3H_8]$ (Cambridge Structural Database (CSD) Refcode: FUYZU01) [20].

the related $Se_2I_4^{2+}$ [17] as well as in the dithionite anion ($S_2O_4^{2-}$) [18,19]. Species of this nature are of particular interest to the present review because they can be regarded as diamagnetic dimers of the $SO_2^{\cdot-}$ and SO_2^- radical ions respectively (Fig. 2).

The propensity for planar organic or light-atom radicals to form π -stacked dimers in the solid state has recently drawn the attention of computational and theoretical chemists interested in modeling unusual bonding phenomena. There is a marked difference in the geometry of the π -stacking interaction that occurs between planar closed-shell organic molecules compared to that occurring between planar π -radicals. When closed-shell (diamagnetic) species form π -stacks, the intermolecular distances tend to be greater

than the sum of van der Waals radii of nearest atoms (ca. >3.4 Å for hydrocarbons) and the molecules tend to be arranged in an “offset” π -stack such that there is both a vertical (perpendicular to the molecular plane) and a horizontal component to the translation from one molecule to its neighbor. Closed-shell organic species that exemplify this type of π -stacking in the solid state include kekulene [22,23], [18]annulene [24], and the low temperature phase of pyrene [25]. The latter is shown in Fig. 3. Hunter and Sanders [26] argue that the offset π -stack geometry can be correlated to a net attraction between the underlying σ -framework (positively charged) of one molecule and the negatively charged π -electron cloud of a neighboring molecule. The σ - π attractions, plus the contribution from van der Waals attractions, must overcome the π - π repulsions. Thus an essentially electrostatic model can be used to understand phenomena such as porphyrin aggregation, intercalation of therapeutics into DNA, and numerous guest–host systems involving planar, resonance-stabilized organic species.

The π -stacking geometry of planar organic or light-atom radicals typically is characterized by intermolecular distances shorter than the sum of van der Waals radii of the closest contact atoms (ca. 2.8–3.3 Å) but markedly longer than a typical single bond. It is frequently a simple vertical translation from one molecule to the next, although it is also common for the molecules to be related by rotation. Typical geometric features of π -stacked paramagnetic planar species are thus noticeably different from those of π -stacked diamagnetic molecules (*vide supra*). Moreover, a π -stacked pair (often called a “dimer”) of two *neutral* radicals exhibits structural features comparable to those of a dimer of two radical *anions* or of two radical *cations*. It is reasonable to conclude that the interaction between planar π -radicals cannot be described by a solely electrostatic model [27]. Furthermore, typical π -stacked dimers of paramagnetic planar species are measurably diamagnetic at or below ambient temperature, implying a strong electronic interaction between the radicals, specifically the formation of an electron-pair (i.e., a bond).

Various descriptive terms for the $mc/2e$ bond in π -stacked dimers have been coined [28,29], none so evocative and succinct as Mulliken and Person’s term, the “pancake bond” [30]. The π -stacked arrangement of molecules is captured by this colorful term, but more importantly, the interaction between large, planar areas of two similar or identical π or π^* frontier molecular orbitals is invoked. In fact, the specific geometries, or π -stacking motifs, of the pancake bonds can almost always be understood in terms of a bonding-type interaction between the singly occupied molecular orbitals (SOMOs). The observed orientation/rotation of one

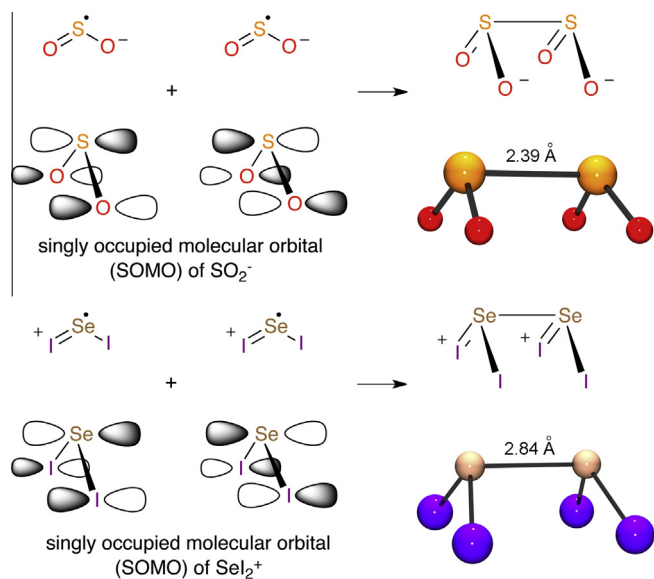


Fig. 2. (Top) $S_2O_4^{2-}$ can be considered a dimer of two $SO_2^{\cdot-}$ radical ions, formed by the interaction of their respective π -systems; image of the solid state structure of $S_2O_4^{2-}$ as found in $ZnS_2O_4 \cdot C_5H_5N$ (CSD Refcode: PYZNDT) [19]. (Bottom) $Se_2I_4^{2+}$ can be considered a dimer of two $SeI_2^{\cdot+}$ radical ions, formed by the interaction of their respective π -systems; image created using the CIF of $[Se_2I_4][Sb_2F_{11}]_2$ (Inorganic Crystallographic Structure Database (ICSD) code 35059) [21].

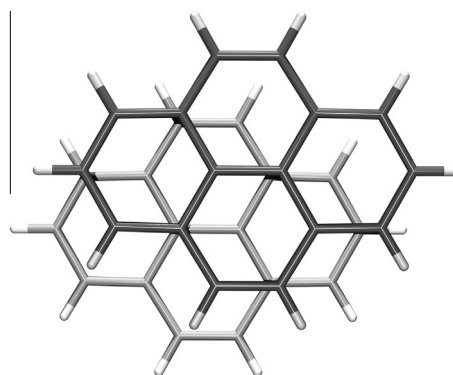


Fig. 3. Image created from the CIF of the low temperature phase of pyrene (CSD Refcode: PYRENE07; data collected at 93 K) [25] showing the offset geometry of the π -stacked pair viewed perpendicular to the molecular plane.

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