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One-Dimensional Metallic Conducting Pathway of Cyclohexyl-Substituted Spiro-Biphenalenyl Neutral Radical Molecular Crystal

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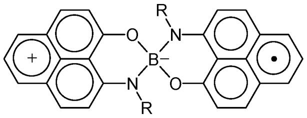
The intriguing idea of intrinsic molecular metals is based on neutral π-radicals.[1] The Haddon group has synthesized a series of spiro-biphenalenyl neutral radicals **1**−**4** with higher conductivities than those of other neutral organic solids.[2−5] Each of these molecules consists of two nearly perpendicular spiro-conjugated phenalenyl moieties but has only one unpaired electron. Their molecular crystals exhibit different packing motifs, such as π-dimers (**1** and **2**),[2] monomers (**3**),[3] and π-steps (**4**),[4] displaying diverse electrical, optical, and magnetic properties.[2−5] The most recently synthesized neutral radical **5** is the best candidate found so far toward the goal of an intrinsic organic molecular metal because the magnetic susceptibility of crystal **5** shows temperature-independent Pauli paramagnetism characteristic of a metal.[6] However, this metallic character is contradicted by a conductivity energy gap of $E_g = 0.11$ eV from resistivity measurements and an optical gap of $E_g = 0.34$ eV from electronic spectroscopy.[6] In this work, we provide the first high quality ab initio electronic structure calculations necessary to better understand this important new member of the neutral radical crystals family. We found that **5** may be considered a quasi one-dimensional (1-D) metal with a 1-D conducting pathway.



1. R = Ethyl
2. R = Butyl
3. R = Hexyl
4. R = Benzyl
5. R = Cyclohexyl

The X-ray crystal structure of **5** is characterized by a π-chain along the [101] direction (Figure 1). Neighboring molecules in the chain adopt a $\pi-\pi$ overlap motif also observed in **1** and **2**;[2] the corresponding interplanar separation in **5** is $D = 3.28$ Å,[6] which is slightly shorter than the van der Waals value and can be attributed to intermolecular covalent bonding due to the unpaired π-electrons in **5**.[7] The D values are uniform and show no sign of a Peierls distortion at the experimental temperature of 223 K. Neighboring chains are parallel in the *ac* plane, with negligible interchain overlap, and are also parallel in the *bc* plane, with one pair of short CC interchain contact (separated by 3.386 Å),[6] similar to the π-step structure observed in **4**.[4] As will be shown next, the interchain overlap along b is very weak, so that the crystal of **5** should be described as a quasi 1-D structure.

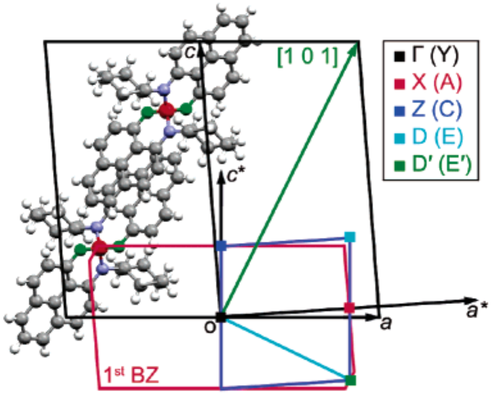


Figure 1. Direct and reciprocal space structure of the monoclinic crystal of **5** viewed along b (b^*). The green arrow indicates the π-chain direction. The reciprocal space vectors carry an $*$. The first Brillouin zone (BZ) is in red. The light blue line represents the reciprocal (101) plane perpendicular to the π-chain. The color codes in the inset indicate the special points in reciprocal space. The points with parentheses are eclipsed by those without.

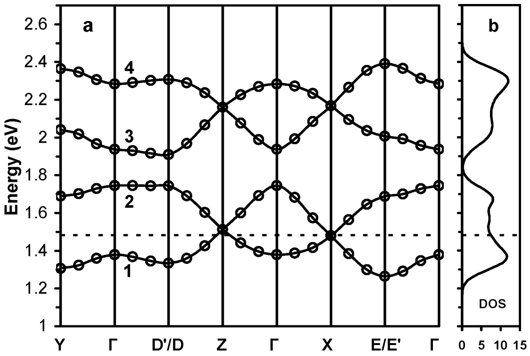


Figure 2. Calculated band structure (a) and density of states (DOS) (b) of **5**. The reciprocal space points are shown in Figure 1 and have the following coordinates: Γ (0,0,0), X (0.5,0,0), Y (0,0.5,0), Z (0,0,0.5), D (0.5,0,0.5), D′ (0.5,0,−0.5), E (0.5,0.5,0.5), and E′ (0.5,0.5,−0.5). Fermi level is indicated by the dashed line.

The band structure in Figure 2 is obtained from density functional solid-state calculations performed on the X-ray structure of **5** using the Vienna ab initio simulation package (VASP)[8] with a PW91 exchange-correlation functional[9] and a plane-wave basis set.[8] Similar to the band structure of **1**,[2,10] the bands shown in Figure 2 are derived from the two phenalenyl moieties for each of the two molecules of **5** in the unit cell, giving four π-bands. We focus only on these π-bands. The ratio of one electron per two phenalenyl moieties leads to a quarter-filled band structure.[2−4] These bands exhibit some symmetry, relating the lower two bands to the upper two bands. The density of states (DOS) shows broadened van Hove singularities, characteristic of quasi 1-D materials.[11]

The bands are very flat along Γ−Y (b^*), indicating that the one pair of CC interchain overlap along b (the same direction as b^*) is weak. The bands are also very flat along Γ−D′. Γ−Y and Γ−D′ define a plane in the reciprocal space with a Miller index (101) with respect to a^*, b^*, and c^* (Figure 1) which is perpendicular to the π-chain.[12] Due to small interchain interactions, the bands should be quite nondispersive along any directions in this reciprocal (101) plane. On the other hand, the bands are quite dispersive along Γ−X and Γ−Z, with a total bandwidth of 0.37 eV for the lower two bands despite the negligible interchain overlap in the *ac* plane. For these two directions, one can decompose the vector into one along the π-chain and the other perpendicular to the π-chain. Therefore,

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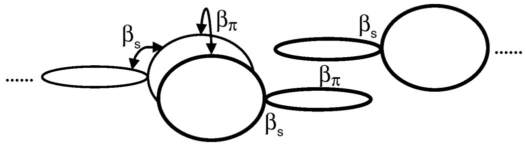

Figure 3. Schematic of a one-dimensional π-chain of **5**; each molecule is represented by two joint ellipses. The effective resonance integrals, β_s and β_π, characterize the intramolecular spiro-conjugation and the intermolecular $\pi-\pi$ overlap, respectively.

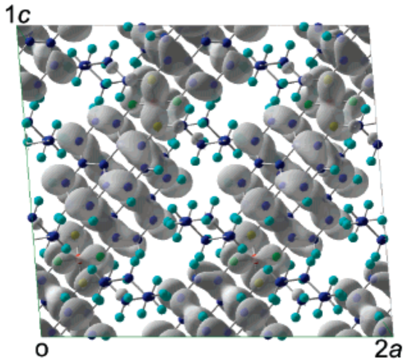

Figure 4. Electron density isosurface of the Kohn−Sham crystal orbital for the second band at the X point viewed along *b*, showing the one-dimensional conducting pathway along the [101] π-chain.

the large dispersion along $\Gamma-X$ or $\Gamma-Z$ can be ascribed to the electron momentum along the π-chain.

The electronic interaction along the π-chain can be approximated by two effective resonance integrals,[13] β_s and β_π, which characterize the intramolecular spiro-conjugation and the intermolecular $\pi-\pi$ overlap, respectively (Figure 3). According to a 1-D Hückel model,[14] the energy expressions for the four crystal orbitals at the Γ point are $(-\beta_\pi - \beta_s)$, $(-\beta_\pi + \beta_s)$, $(\beta_\pi - \beta_s)$, and $(\beta_\pi + \beta_s)$, respectively, from which we obtained $\beta_s = 0.18$ eV and $\beta_\pi = 0.27$ eV. The β_s value thus estimated is approximately equal to the value of 0.19 eV obtained from monomer calculations of **5**,[15] justifying the validity of the 1-D Hückel model.

Figure 4 shows the electron density isosurface of the Kohn−Sham crystal orbital for the second band at the X point, which provides a pictorial representation of the 1-D conducting pathway only along the [101] π-chain. It indicates a negligible interchain overlap, explaining the small bandwidths perpendicular to the chain (Figure 2). Therefore, conduction might follow a hopping mechanism in the perpendicular directions.[16] Despite the large dispersions along $\Gamma-X$ or $\Gamma-Z$, conduction along these directions is hampered by the hopping of charge carriers between chains.

Pauli paramagnetism provides a DOS at the Fermi level of $N(E_f) = 15.5$ states eV^{-1} molecule^{-1}.[6] As shown in Figure 2, the Fermi level passes through the lower two bands, corresponding to the quarter-filled band structure (metallic character), in agreement with experimentally observed Pauli paramagnetism. The DOS at the Fermi level from our calculations is $N(E_f) = 7.5$ states eV^{-1}, which can be converted to 3.8 states eV^{-1} molecule^{-1} to compare with the experimental value. Such large discrepancy is very common in other organic molecular crystals.[17] The value of $N(E_f) = 8.0$ states eV^{-1}molecule^{-1} calculated from extended Hückel theory (EHT)[6] is larger than our value by a factor of ∼2, but the Fermi level by EHT is located at the single peak of the DOS curve,[6] while in our calculations, the Fermi level is located at the valley between two peaks of the DOS curve.

Transmission electronic spectroscopy of **5** provides an optical "gap" of $E_g = 0.34$ eV. This "gap" compares well with the calculated energy difference between the lower two bands at the Γ point (0.366 eV), or the peak-to-peak gap on the DOS curve (0.30 eV) (Figure 2), supporting the quarter-filling scenario. Further support for quarter filling comes from the metallic character as indicated by the absence of an onset electronic transition. In contrast to **5**, for the other members of the series (**1**−**4**), the onset of the electronic transitions was identified from the electronic spectra at high transmittance.[3−5,10]

The room-temperature conductivity along the needle axis of **5** reaches $\sigma_{RT} = 0.3$ S cm^{-1}, the highest value among the neutral radical conductors. Single-crystal resistivity measurement along the needle axis of **5** indicates a semiconductor behavior with a gap of $E_g = 0.11$ eV. This behavior remains puzzling until further experimental data become available. We note that the needle axis of crystal **5** is not the π-chain direction.[18] Along any directions other than the π-chain, conduction is impeded by the small interchain overlap.

In summary, we have found theoretical evidence that the neutral radical crystal **5** has a 1-D metallic conducting pathway along the [101] π-chain consistent with its optical and magnetic properties. More detailed understanding of the electrical property will require further experimental and theoretical work.

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Supporting Information Available: Electron density isosurfaces of crystal orbitals at the Γ and X points, molecular calculations of β_s, geometries used for molecular calculations, derivation of energy expressions for crystal orbitals at the Γ point, and complete ref 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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