

**MULTICENTER COVALENT PI-PI BONDING INTERACTION AND ITS ROLE
IN THE SOLID-STATE PROPERTIES OF PHENALENYL-BASED
ORGANIC RADICAL MATERIALS**

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By

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ABSTRACT

We focus on phenalenyl-based organic radical materials including 2,5,8-tri-*tert*-butylphenalenyl radical, spiro-biphenalenyl (SBP) radicals, cyclo-biphenalenyls, and biphenalenyl biradicals (BPBRs) with an *s*-indacene linkage in pursuit of multicenter covalent pi-pi bonding interaction and its effects. The building blocks of these materials are characteristic of unpaired electrons associated with structural phenalenyl units.

A number of experimental properties from literature have been employed including NMR, angle-resolved photoelectron spectroscopy (ARPES), magnetism of molecules, dimers, and of one-dimensional (1-D) chains, electrical conduction, etc. Magnetic susceptibilities have been analyzed using Bleaney-Bowers dimer model, alternating chain model, and Curie-Weiss model. A theoretical framework based on molecular orbital theory and Hubbard dimer model has been established to analyze the magnetic properties. These physical properties have been interpreted using our quantum mechanical calculations including molecular, dimer, and solid-state calculations. Theories employed span from semiempirical theories, density functional theories (DFT), Hartree-Fock (HF), to correlation calculations including outer valence Green's function (OVGF) and wave function stability analysis. A gamut of Gaussian and plane-wave basis sets have been used.

Extensive numerical studies have been performed to investigate the dependence of transfer integrals on basis set, level of theory, and intermolecular packing through a dimer approach. Validation through experimental results of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-dithiole) (BTQBT), K-TCNQ, and hexagonal graphite shows that DFT in one of its presently popular forms, such as PW91, in combination with double zeta plus polarization Gaussian basis sets or alternatively with moderate size plane-wave basis sets provides reliable transfer integrals, and therefore can serve as a basis for energy band calculations.

Multicenter covalent pi-pi bonding has been identified as a novel and important intermolecular bonding interaction. It manifests in various ways for the phenalenyl-based organic radical materials: it leads to an usual pi-pi bonded intermediate in the Cope rearrangement of the cyclo-biphenalenyl; it drives a subtle change of molecular geometries for the BPBRs; it is responsible for the self association of SBPs into diverse aggregations such as pi-dimers and pi-chain; and in the case of cyclohexyl-SBP pi-chain, it leads to an efficient electron delocalization along the chain and a metallic conduction according to the band calculations using the validated theory.

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Table of Contents

Chapter 1. Intrinsic Metallic Conductor Based on Neutral Organic Compounds: Another Milestone of Organic Metals?.....	1
Chapter 2. Intermolecular Transfer Integrals for Organic Molecular Materials: Can Basis Set Convergence be Achieved?.....	8
Chapter 3. Validation of Intermolecular Transfer Integral and Bandwidth Calculations for Organic Molecular Materials.....	24
Chapter 4. Electronic Structures and Charge Transport Properties of the Organic Semiconductor BTQBT and Its Derivatives.....	55
Chapter 5. Spin Crossover of Spiro-Biphenalenyl Radical Conductors: a Tentative Explanation.....	84
Chapter 6. Intermolecular Covalent π - π Bonding and Magnetic Properties of Phenalenyl and Spiro-Biphenalenyl Radical π -Dimers.....	92
Chapter 7. Stepwise Cope Rearrangement of Cyclo-biphenalenyl: a Side Story of Multi-center Covalent π - π Bonding Interaction.....	139
Chapter 8. Energy Bands, Magnetism, and Bond Distances Indicate Intermolecular Covalent π - π Bonding in Biphenalenyl Biradicaloid Molecular Crystal.....	173
Chapter 9. One-Dimensional Metallic Conducting Pathway of Cyclohexyl-Substituted Spiro-Biphenalenyl Neutral Radical Molecular Crystal.....	??
Chapter 10. Concluding Remarks.....	??