Singlet Biradicals

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Resonance Balance Shift in Stacks of Delocalized Singlet Biradicals**

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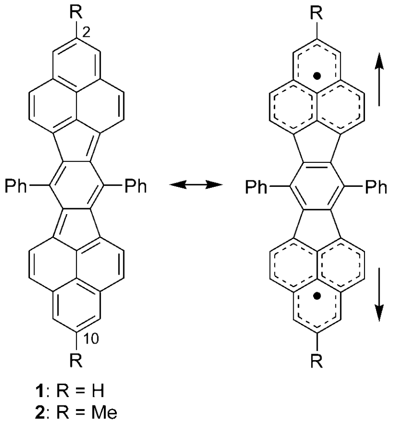
Dedicated to Professor Ichiro Murata on the occasion of his 80th birthday

Recently we succeeded in the isolation of delocalized singlet biradicals[1,2] utilizing the spin-delocalizing character of the phenalenyl radical.[3] We demonstrated that the singlet biradical **1** has strong spin–spin interactions between molecules through the overlap of phenalenyl rings in the one-dimensional (1D) chain even though the closed-shell Kekulé structure **1** can be drawn as a resonance contributor (Scheme 1).[1b] Huang and Kertesz gave further insight into the spin–spin interactions from a theroretical point of view and showed that the spin–spin interaction between the molecules was predicted to be stronger than that within the molecule.[4] These experimental and theoretical findings are associated with very fundamental issues: Do delocalized singlet biradicals actually have open-shell character? Are the electrons coupled within a molecule involved in covalent bonding between molecules? In this study we will demonstrate that intra- and intermolecular spin–spin interactions strongly correlate and can be altered in magnitude by an applied external field. Our proposal is based on the experimentally determined molecular structure of **2**, a temperature-dependent reflection spectrum of **2**, and a pressure-dependent reflection spectrum of **1**. Methyl groups at the 2- and 10-positions in **2**, where the frontier molecular orbital has very small coefficients, are expected to alter the distance between the overlapping phenalenyl rings with respect to the analogous separation in **1**, and as a result, the magnitude of the intermolecular spin–spin interaction should be affected.



Scheme 1. Resonance structures of **1** and **2**. The arrows in the biradical structure represent antiparallel spins.

The synthesis of **2** is outlined in Scheme 2. The 3,10- and 3,11-bis(bromomethyl) compounds **3** were synthesized according to the previously reported procedures.[1b] The individual isomers were not isolated because both were expected to lead to the single compound **2**. Bis(2-methylpropionic acid) derivatives **5** were obtained in three steps by standard methods. Friedel–Crafts cyclization of the acyl chloride derivatives of **5** with $AlCl_3$ afforded diketones **6**. These were reduced with $NaBH_4$ and subsequently dehydrated with a catalytic amount of *p*-toluenesulfonic acid to afford the dihydro compounds **8**. Dehydrogenation of **8** with *p*-chloranil afforded the hydrocarbon **2** as green prisms. Compound **2** was found to be stable in the solid state at room temperature.

The small HOMO–LUMO gap of **2**, which is an essential factor for a singlet biradical electronic structure, was confirmed by electrochemical and optical methods. The cyclic voltammogram of **2** shows four reversible redox waves: $E_2^{ox} = +0.51$, $E_1^{ox} = +0.11$, $E_1^{red} = -1.09$, and $E_2^{red} = -1.62$ (V vs. ferrocene/ferrocenium couple (Fc/Fc$^+$), see Figure S1 in the Supporting Information), which led to an electrochemical HOMO–LUMO gap of 1.20 eV. The electronic absorption spectrum of **2** in CH_2Cl_2 shows an intense low-energy band at 756 nm ($13\,200\ cm^{-1} = 1.64$ eV, $\varepsilon = 115\,000$, $f = 0.605$, see

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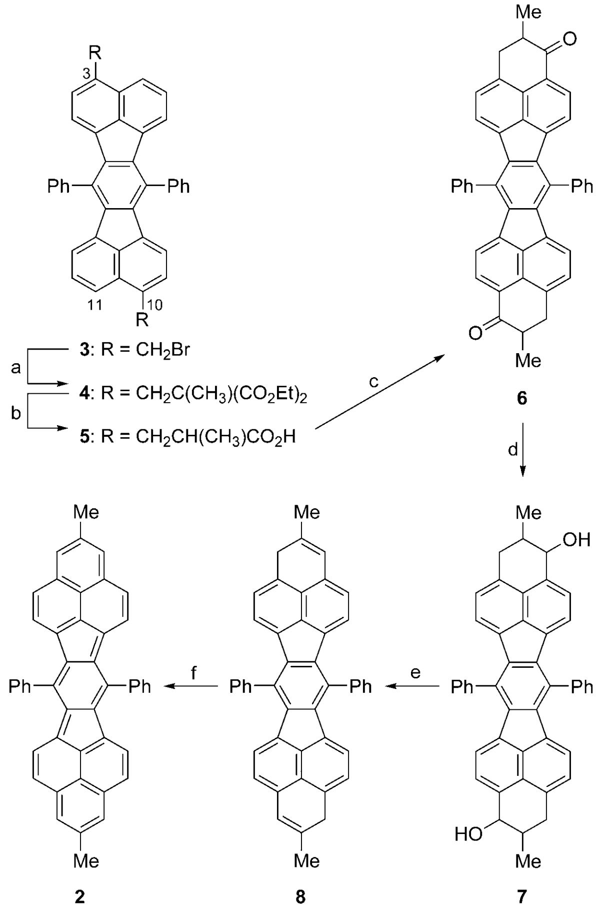

Scheme 2. Synthesis of **2**. a) $CH_3CH(CO_2Et)_2$, EtONa, EtOH/toluene (1:2), room temperature, 51 %; b) 1. aq KOH, EtOH, reflux, 2. aq HCl, reflux, 87 %; c) 1. $(COCl)_2$, reflux; 2. $AlCl_3$, CH_2Cl_2, $-78\rightarrow 20\,^\circ C$, 25 %; d) $NaBH_4$, $EtOH/CH_2Cl_2$ (5:2), room temperature, 99 %; e) cat. *p*-toluenesulfonic acid, toluene, 90 °C, 90 %; f) *p*-chloranil, toluene, 90 °C, 60 %.

Figure 3). These values are almost the same as those of **1**, indicating that the methyl substituents in **2** have a minimal effect on the electronic structure. Thus **2** possesses biradical character identical to that of **1** (30 % at the CASSCF(2,2)/6-31G level of calculation).[1b] ^1H NMR spectrum of **2** at −30 °C displays sharp signals. This finding indicates that **2** behaves intrinsically as a closed-shell molecule in the single-molecule state. Upon heating, the signals of the ring protons, but not the phenyl groups, undergo progressive line broadening (see Figure S2 in the Supporting Information). Similar results have been obtained for **1**, and the broadening at elevated temperatures is ascribed to triplet species that are thermally accessible as a result of the small HOMO–LUMO energy gap.

Fortunately, we could obtain many kinds of polymorphic crystals of **2**, which included solvent molecules and were suitable for X-ray crystallographic structure analysis, by recrystallization from chlorobenzene (PhCl), benzene, or toluene solutions (see Figures S3–5 and Table S1 in the Supporting Information). In the crystal of **2**/PhCl, the methyl groups are effective in controlling the π–π separation distance of the overlapping phenalenyl rings (Figure 1). Compound **2** forms a 1D π–π chain with superimposed π–π overlap at the phenalenyl rings.[5] This stacking pattern is quite similar to that of **1** except for larger intermolecular π–π separation (3.225 Å for **2** vs. 3.137 Å for **1** at 200 K), which is nevertheless shorter than sum of the van der Waals contacts of carbon atoms (3.4 Å). The average intermolecular π–π distance decreased upon cooling from room temperature: 3.279 Å (300 K), 3.225 Å (200 K), and 3.208 Å (100 K). Interestingly, there is a strong correlation between the π–π separation distance and the length of bond **a** (Figure 2 a).[6] As shown in Table 1, the shorter the π–π separation, the greater the length of bond **a**. This result indicates that the intra- and intermolecular spin–spin interactions strongly correlate in the 1D chain. A decrease in the π–π separation distance enhances the intermolecular orbital overlap and strengthens the intermolecular bonding interaction. The enhanced intermolecular interaction makes the unpaired electrons more localized on the phenalenyl rings and consequently weakens the intramolecular bonding interaction.

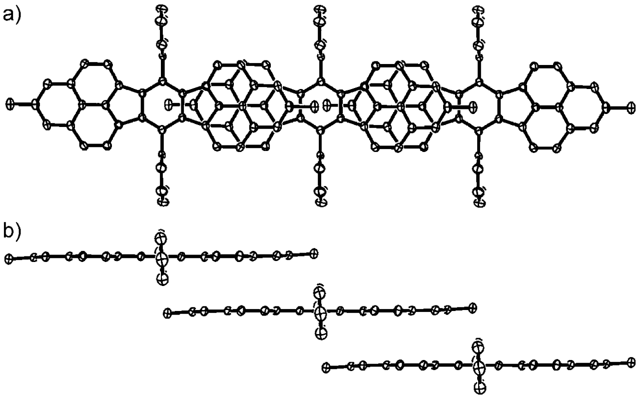

Figure 1. Top view (a) and side view (b) of the 1D chain of **2**/PhCl at 200 K. Hydrogen atoms and chlorobenzene solvent molecules are omitted for clarity. Ellipsoids are shown at the 50 % probability level.

Table 1: The π–π separation distances (*R*) between stacked phenalenyl rings and the lengths (*L*) of bond **a** in crystals of **2** with various solvent molecules and at various temperatures.

	Benzene	PhCl	PhCl	PhCl	Toluene
T [K]	200	100	200	300	200
R [Å]	3.160	3.208	3.225	3.279	–
L [Å][a]	1.476(2)	1.472(2)	1.469(2)	1.465(3)	1.457(2)

[a] Mean values.

The strongest intermolecular spin–spin interaction for **2** was found in the crystal of **2**/benzene. Here, **2** also forms a 1D π–π chain with the superimposed phenalenyl rings and considerably short average π–π distances (3.160 Å at 200 K).[7] The strongest intermolecular interaction results in the longest bond **a**, fully consistent with the findings in **2**/PhCl. It is noted that in the crystals of **2**/PhCl and **2**/benzene the spin–spin interaction is restricted to within the 1D chains as a result of the lack of effective π–π overlap between the chains. Fortunately, a zero-limit of intermolecular spin–spin interaction could be found in the crystal of **2**/toluene. Individual

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molecules of **2** were isolated because the toluene solvent molecules prevent effective π–π overlap between phenalenyl rings. Therefore the bonding interaction of the unpaired electrons on phenalenyl radicals is restricted to within the molecule. Bond **a** in **2**/toluene is the shortest among the polymorphic crystals of **2**.

Based on these results, the electronic structure of the 1D chain is best rationalized in terms of the Resonating Valence-Bond (RVB) model proposed by Pauling[8] and Anderson.[9] This model describes a Li–Li bond as a resonating singlet pair of two electrons. By replacing the lithium atom by the phenalenyl radical, we can apply the model to represent the intra- (**A**) and intermolecular (**B**) bonding in the 1D chain of **2**. The electronic structure of the 1D chain can be described as the superposition of formulas **A** and **B**. (Figure 2 b).[10] The shorter distance between overlapping phenalenyl rings gives greater weight to formula **B** in the electronic structure of the 1D chain. This "resonance balance shift" to formula **B** at lower temperature results in weaker bonding interaction within the molecule, that is, the greater length of bond **a**.

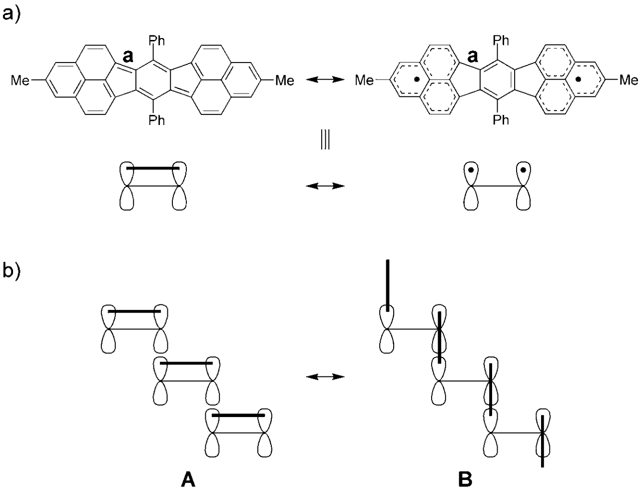

Figure 2. a) Schematic drawing of the resonance structures of a single molecule of **2**. b) The RVB model for the electronic structure in the 1D chain of **2**.

The resonance balance shift in the 1D chain is related to the temperature- and pressure-dependent electronic spectra observed with single crystals of **2**/PhCl and **1**/PhCl. In the reflection spectrum of a single crystal of **2**/PhCl (Figure 3) the absorption band is shifted to substantially lower energy with respect to the band recorded for the solution of **2** in CH_2Cl_2, as observed in **1**/PhCl.[1b] This finding indicates that the electronic structure of the molecule is affected by the strong intermolecular spin–spin interaction in the 1D chain. Upon cooling, the lowest energy band of **2**/PhCl shifts to the higher energy region, contrary to our expectation. Figure 4 shows the temperature dependency of the lowest-energy reflection bands recorded on a single crystal of **2**/PhCl. In addition, the pressure-dependent reflection spectra of a single crystal of **1**/PhCl showed a similar higher energy shift of the lowest energy band (see also Figure S6 in the Supporting Information).[11]

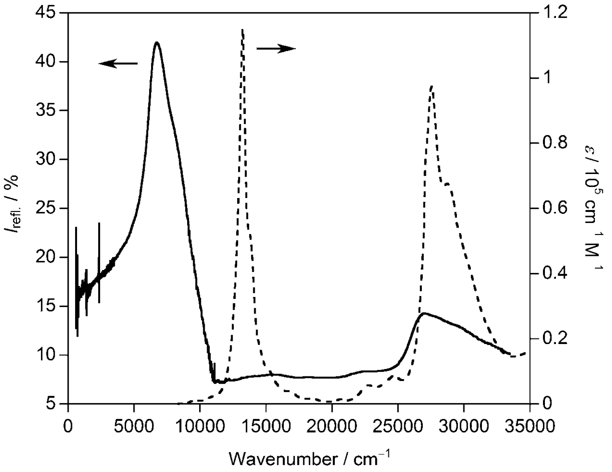

Figure 3. Optical spectra of **2**. Absorption spectrum of a solution of **2** in CH_2Cl_2 (dashed line) and reflection spectrum (solid line) of a single crystal of **2**/PhCl at 300 K obtained with light polarized along the *c* axis.

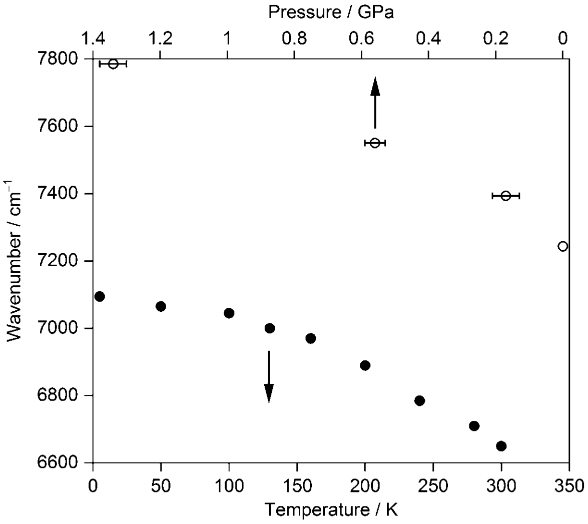

Figure 4. Temperature dependency of the energy of the lowest energy reflection bands on a single crystal of **2**/PhCl (black circles) at ambient pressure, and pressure dependency of the energy of the lowest energy reflection bands on a single crystal of **1**/PhCl (open circles) at room temperature.

The coexistence of intra- and intermolecular spin–spin interactions in **2**/PhCl and **1**/PhCl indicates that their 1D chains mimic the electronic structure of an infinite polyene, although the magnitude of the bonding interactions of unpaired electrons are quite different (0.2–0.3 eV for **1**[4] vs. 2.0–2.4 eV for an infinite polyene[12]). As stated in reference [12], individual double bonds in an infinite polyene are corresponding to "molecules" and single bonds to weak intermolecular orbital overlap in a 1D molecular crystal composed of a closed-shell compound. Following this simple model, we initially expected a lower energy shift of the lowest energy band with more effective intermolecular orbital overlap caused by decrease of the π–π separation distance, because **2** and **1** seem to be intrinsically closed-shell

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compounds, at least in the single-molecule state according to the ^{1}H NMR results. Consequently their 1D chains should have stronger intramoleculer spin–spin interactions perturbed by weaker intermolecular interactions. The experimental results strongly contradict our expectation, which suggests that the 1D chain of **2** and **1** has stronger interactions between the molecules than within individual molecules. In other words, the "double bond" can be drawn in the phenalenyl overlap and the "single bond" within the molecule. In the 1D chains, the contribution weight of formula **B** is unexpectedly large even at atmospheric pressure, and the resonance balance shift to formula **B** induced by lowering temperature or applying pressure to the crystal results in a larger "bond alternation" of the electronic structure, that is; more "double-bond" character in the phenalenyl overlap. The larger "bond alternation" causes a greater separation in energy between the HOMO and LUMO of the 1D chains and thus the higher energy shift of the lowest energy band is observed.[13]

In conclusion, we have synthesized the delocalized singlet biradical **2** consisting of two phenalenyl rings. We determined that the intra- and intermolecular spin–spin interactions correlate in the π–π 1D chains and that the electronic structure of the 1D chain is best represented by the RVB model. Understanding the interaction of two electrons is fundamental to understanding the covalent bond itself. In this view our singlet biradical molecules provide the fundamental insight that an intermediate bonding interaction of two electrons can lead to bifunctionality in covalent bonds in molecular systems, that is, the coexistence of intra- and intermolecular chemical bonding.

Experimental Section

Detailed synthetic procedure and crystallographic data of **2** are described in the Supporting Information. CCDC 731071 (**2**/benzene), 731072 (**2**/PhCl at 100 K), 731073 (**2**/PhCl at 200 K), 731074 (**2**/PhCl at 300 K), and 731075 (**2**/toluene) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[6] The length of bond **a** would be the most sensitive to the contribution weight of the each canonical structure in Figure 2 a, because bond **a** has both single- and double-bond character in the Kekulé structures but only single-bond character in the biradical structure.

[7] No changes in the average intermolecular π–π distances were observed in crystals of **1**/PhCl upon cooling (3.137 Å at 200 K and 290 K).

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[10] A resonating valence-bond ground state in a phenalenyl-based neutral radical conductor was proposed in reference [5c].

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[11] We used a single crystal of **1** for the pressure-dependent experiment, because the methyl groups of **2** might sterically hinder the closer approach of the phenalenyl rings under high pressure.

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[13] Alternatively, the electronic structure of the 1D chains can be described by the antiferromagnetic 1D Heisenberg chain model for the system with two spin–spin interactions, $J1$ and $J2$, as mentioned in reference [4]. Absorption energy in the solid state would depend on the balance in the strengths of $J1$ and $J2$ and might approach a zero-limit in the case of $J1 = J2$ (no bond alternation). The absorption energy increases with the unbalance of $J1$ and $J2$ ($J1 > J2$ or $J1 < J2$). If $J1$ and $J2$ are taken as intra- and intermolecular spin–spin interactions, respectively, the former case is found in crystals of most closed-shell compounds and $J1$ is usually much greater than $J2$, but surprisingly our singlet biradical compounds were found to correspond to the latter case.

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