Radicals

DOI: 10.1002/ange.200502303

Synthesis, Intermolecular Interaction, and Semiconductive Behavior of a Delocalized Singlet Biradical Hydrocarbon**

Takashi Kubo, Akihiro Shimizu, Maki Sakamoto, Mikio Uruichi, Kyuya Yakushi, Masayoshi Nakano, Daisuke Shiomi, Kazunobu Sato, Takeji Takui, Yasushi Morita, and Kazuhiro Nakasuji**

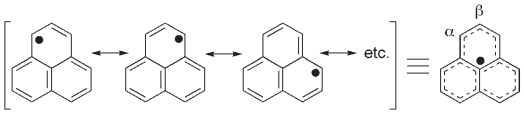
Most Kekulé hydrocarbons, which are characterized by a closed-shell electron configuration, accommodate their π electrons only in bonding orbitals and consequently are quite stable. In general, such stable Kekulé compounds have wide HOMO–LUMO gaps, and their electronic structures in the ground state can be well described by a single electron configuration $^1\Phi_0$. In contrast, some Kekulé compounds, such as quinoid hydrocarbons, have a relatively small HOMO–LUMO gap, which leads to an admixture of a doubly excited configuration $^1\Phi_{H,H\rightarrow L,L}$ into the ground configuration $^1\Phi_0$ in the description of the ground state.[1a] As a result of this configuration mixing, the repulsion between the two electrons is taken into consideration and the two electrons with antiparallel spins are permitted to correlate in separate spaces. This electron correlation diminishes the bond covalency and increases the biradical character of the system.

[*] Dr. T. Kubo, A. Shimizu, M. Sakamoto, Prof. Dr. Y. Morita, Prof. Dr. K. Nakasuji
Department of Chemistry
Graduate School of Science
Osaka University
Machikaneyama 1-1, Toyonaka, Osaka 560-0043 (Japan)
Fax: (+81) 6-6850-5395
E-mail: kubo@chem.sci.osaka-u.ac.jp
nakasuji@chem.sci.osaka-u.ac.jp
Dr. M. Uruichi, Prof. Dr. K. Yakushi
Department of Applied Molecular Science
Institute for Molecular Science
Okazaki 444-8585 (Japan)
Prof. Dr. M. Nakano
Department of Materials Engineering Science
Graduate School of Engineering Science
Osaka University
Toyonaka, Osaka 560-8531 (Japan)
Prof. Dr. D. Shiomi, Prof. Dr. K. Sato, Prof. Dr. T. Takui
Departments of Chemistry and Materials Science
Graduate School of Science
Osaka City University
Sumiyoshi-ku, Osaka 558-8585 (Japan)

[**] This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 17550034, and Area No. 769, Proposal No. 15087202) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

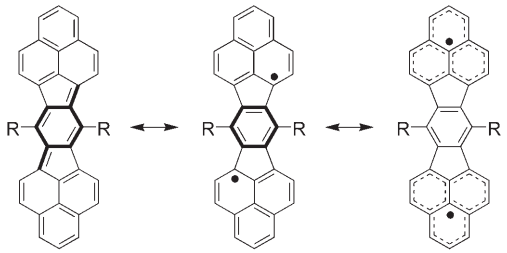
The quinoidal Kekulé hydrocarbons are highly reactive and easily dimerize or polymerize at normal temperature.[2] Such behavior is strongly reminiscent of radical reactivity. Related interesting reactivity has been observed for pleiadene, which dimerizes readily even at 110 K through a two-step cycloaddition or a symmetry-forbidden [4s + 4s] concerted process.[1] The latter process is predicted to be related to the $^1\Phi_{H,H\rightarrow L,L}$ configuration. The biradical-like reactivity implies strong intermolecular interactions in the ground state, which would be a most remarkable feature for singlet biradical compounds. However, great difficulties are encountered in estimating the intermolecular interaction due to the instability. Although kinetically stabilized singlet biradicals such as Chichibabin's hydrocarbon have been isolated and characterized, sterically crowded structures mask the effective intermolecular π–π interactions.[3] To estimate the intermolecular interactions, thermodynamic stabilization of the singlet biradicals would be required instead of kinetic stabilization. One of the most effective means of thermodynamic stabilization is delocalization of unpaired electrons. Herein, we focus on phenalenyl radical as a highly spin-delocalized molecule (Scheme 1). The radical is known to be



Scheme 1. Spin delocalization of phenalenyl radical.

persistent, and many related compounds have been isolated.[4] We report the synthesis and isolation of a singlet biradical utilizing the highly spin delocalizing property of the phenalenyl radical. Furthermore, we present the intermolecular interaction and solid-state properties of a delocalized singlet biradical.[5]

For the purpose of estimating the intermolecular interaction, we focused on a closed-shell conjugated system that contains the phenalenyl radical structure.[6] Hydrocarbon **1a** consists of *p*-quinodimethane and two phenalenyl moieties.[7] The quinoid Kekulé compound **1a** would resonate well with biradical structure **1a**′ as a result of gaining the aromatization energy of the central six-membered ring (Scheme 2). The unpaired electrons emerging on the terminal carbon atoms of the *p*-quinodimethane moiety can delocalize on the phenalenyl rings (structure **1a**″). This consideration of resonance



1a: R = H
1b: R = Ph
1'
1''

Scheme 2. Resonance structures of **1**.

structures leads to the conclusion that **1a** would be a thermodynamically stabilized singlet biradical. Quantum chemical calculations on **1a** strongly support the biradical character. A CASSCF(2,2)/6-31G//RB3LYP/6-31G** calculation gave an admixture of 15% of the doubly excited configuration $^1\Phi_{H,H\rightarrow L,L}$ into the singlet ground state. A broken-symmetry UB3LYP/6-31G** calculation also gave a similar biradical character; the natural orbital occupation number (NOON)[8] of the LUMO was 0.37, and the spin contamination $\langle S^2\rangle = 0.65$ (see Supporting Information). Thus, the singlet biradical character of **1a** is estimated to be 30–37%.

The synthetic procedure for the diphenyl derivative **1b** is shown in Scheme 3. The key intermediates **4** were obtained as a mixture of 3,10- and 3,11-dimethyl isomers by Diels–Alder reaction between **2** and **3** followed by decarbonylation and dehydration with *p*-chloranil. Individual isomers were not isolated for further transformations because the two isomers can lead to a single compound **1b**. Bis(propionic acid) derivatives **7** were obtained in three steps. Intramolecular Friedel–Crafts cyclization of the acyl chloride of **7** with $AlCl_3$ gave diketone **8**, which was reduced and subsequently dehydrated to afford dihydro compound **10**. Dehydrogenation of **10** with *p*-chloranil provided the target compound **1b** as dark green plates. Compound **1b** was found to be stable in the solid state at room temperature, even in air.

As mentioned above, a small HOMO–LUMO gap is an essential factor for a singlet biradical electronic structure. The small HOMO–LUMO gap of **1b** was confirmed by electrochemical and optical methods. The cyclic voltammogram of **1b** gave an irreversible oxidation wave ($E^{ox}_{pa} = +0.08$ V vs ferrocene/ferrocenyl couple (Fc/Fc^+)) and a quasi-reversible reduction wave ($E^{red}_{1/2} = -1.07$ V vs Fc/Fc^+), which led to an electrochemical energy gap (HOMO–LUMO gap) of approximately 1.1 eV. The electronic absorption spectrum of **1b** in CH_2Cl_2 showed an intense low-energy band at 746 nm ($\varepsilon = 178\,000$, $f = 0.649$). An INDO/S configuration interaction (CI) calculation suggested that the low-energy band could be assigned to a symmetry-allowed B_{3u} HOMO–LUMO transition. These findings indicate an optical energy gap of 1.66 eV for **1b**. The small HOMO–LUMO gap is ascribable to the nonbonding character of the frontier orbitals, as shown in Figure 1. The frontier orbitals of **1a** retain the nonbonding

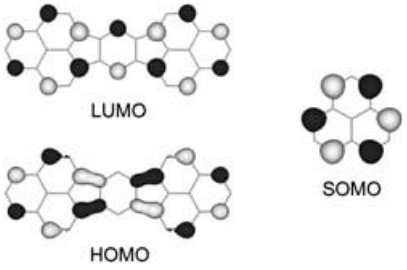
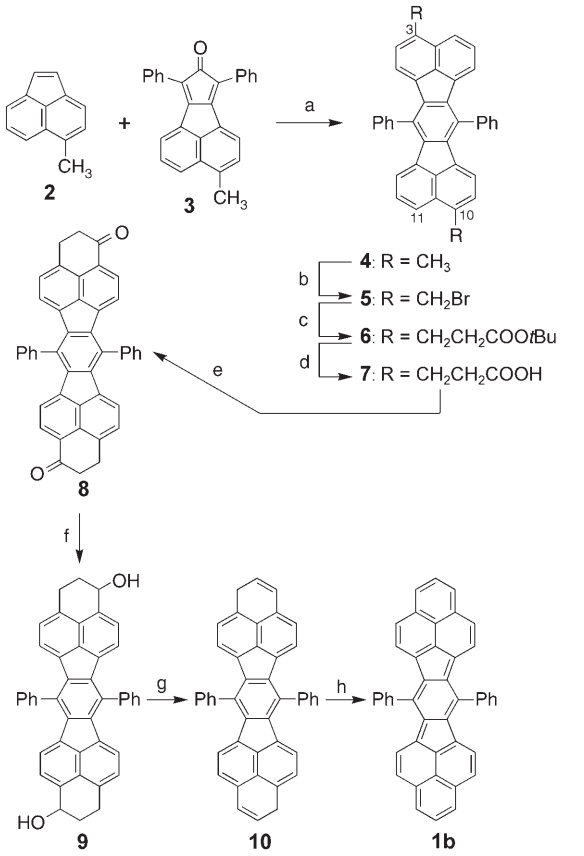


Figure 1. The HOMO and LUMO of **1a**, and the SOMO of the phenalenyl radical.

character of the singly occupied molecular orbital (SOMO) of the phenalenyl radical. The most important feature is a quite large spatial overlap between HOMO and LUMO. The large spatial overlap and small energy gap are responsible for the admixture of a doubly excited configuration into the ground state, that is, a singlet biradical character.[9]

Recrystallization of **1b** from a solution in chlorobenzene gave relatively large single crystals ($1 \times 0.3 \times 0.2$ mm^3), including chlorobenzene molecules of solvation, which were analyzed by X-ray diffraction. As shown in Figure 2, **1b** forms one-dimensional (1D) chains with a slipped stacking arrangement and an average π–π distance of 3.137 Å,[10] which is substantially shorter than the van der Waals contact of carbon atoms (3.4 Å). The π–π overlap was found only on phenalenyl moieties in the same arrangement as that of the phenalenyl radical dimer.[4a] The staggered stacking of the radical dimer maximizes the SOMO–SOMO interaction between radicals, and the overlap of SOMOs is one of the crucial attractive bonding interactions.[11] The dominant attractive force for **1b** would originate from the bonding interaction between the unpaired electrons that appear in the singlet biradical canonical structure **1b**″, in addition to a general attractive dispersion force. In the valence bond description, the interaction of the two unpaired electrons could be repre-



Scheme 3. Synthesis of **1b**. a) Xylene, reflux, 83%; b) NBS, benzoyl peroxide (cat.), benzene, reflux, 99%; c) $CH_3COOtBu$, LDA, THF, −78→−30°C, 66%; d) *p*-toluenesulfonic acid (cat.), benzene, reflux, 98%; e) 1) $(COCl)_2$, reflux; 2) $AlCl_3$, CH_2Cl_2, −78→−30°C, 88%; f) $NaBH_4$, EtOH + CH_2Cl_2, room temperature, 95%; g) *p*-toluenesulfonic acid (cat.), benzene, reflux, 89%; h) *p*-chloranil, benzene, reflux, 99%. NBS = *N*-bromosuccinimide, LDA = lithium diisopropylamide.

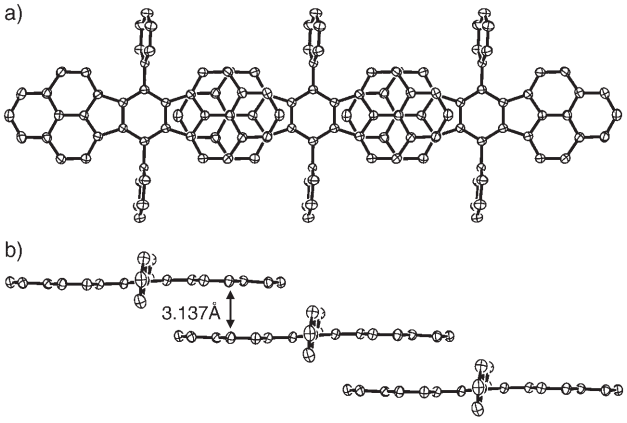


Figure 2. Crystal structure of **1b**. Hydrogen atoms and the solvated chlorobenzene molecule are omitted for clarity.

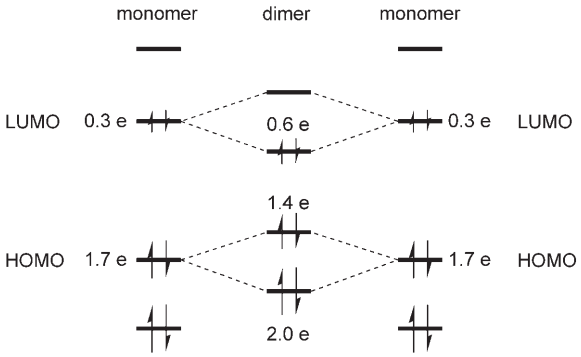
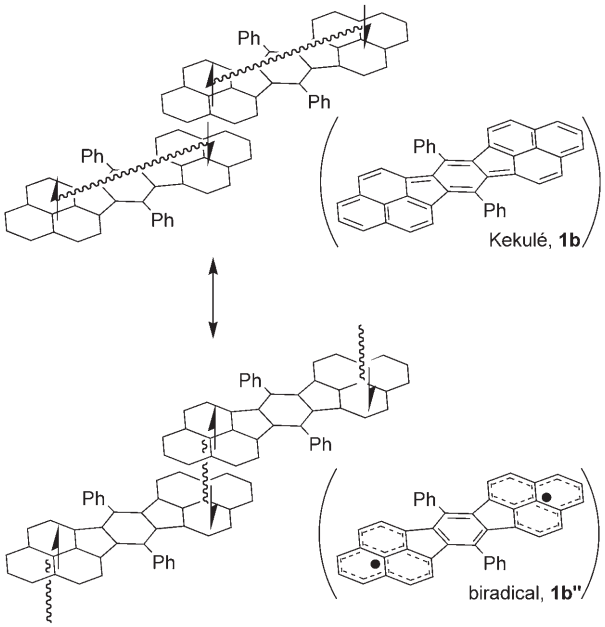


Figure 3. Schematic drawing of the molecular orbital interaction of dimeric **1a** through the doubly excited configuration $^1\Phi_{H,H\rightarrow L,L}$.

sented by the resonance between intra- and intermolecular interaction, as shown schematically in Scheme 4. Thus, a strong intermolecular covalent character is a characteristic



Scheme 4. Resonance structures of intra- and intermolecular interactions of two unpaired electrons in the 1D chain. Wavy lines denote electron–electron interactions. In parentheses: best descriptions of the electronic structure in each resonance state.

feature of singlet biradicals. A restricted Hartree–Fock (RHF) plus CI method is useful for understanding the intermolecular covalency. For simplicity, the following discussion focuses on a dimer of **1b**, which is the smallest unit of the 1D chain. As described above, **1b** has a biradicaloid ground state with 15% of the doubly excited configuration as a result of the configuration interaction between HOMO and LUMO. The interaction between the partially occupied HOMOs would lead to the partially occupied "HOMO" of the dimer (1.4 e), as shown in Figure 3. The partial occupancy suppresses a four-electron repulsion generally arising from the interaction between fully occupied orbitals. The LUMO–LUMO interaction would also contribute to stabilization of the system, because a newly formed "LUMO" of the dimer, which is more strongly stabilized than the original LUMO, can accommodate 0.6 electrons.[12] The presence of the well-stabilized intermolecular orbitals would indicate intermolecular covalency.

The electrical conductivity of a compressed pellet of doubly recrystallized **1b** was measured by a two-probe method. The room-temperature conductivity was $1.0\times10^{-5}\,S\,cm^{-1}$ with an activation energy of 0.3 eV at 200–300 K (see Supporting Information). The conductivity of a single crystal along the stacking direction (*b* axis) was slightly larger ($5.0\times10^{-5}\,S\,cm^{-1}$ at room temperature) than that of the powdered sample. To the best of our knowledge, **1b** shows the best single-component conductivity among structurally well-defined hydrocarbon molecules in a neutral state.[13] To estimate the electronic structure in the solid state, we performed band-structure calculations using extended Hückel theory (EHT) on the crystal structure of **1b**.[14] The dispersions of valence and conduction bands were found to be substantial (0.54 and 0.51 eV, respectively) along the π–π stacking direction (*Y*), whereas only slight dispersions were seen along *X* (Figure 4).[15] The dispersion along *Z* (0,0,1/2) should be very small as a result of the presence of chlorobenzene of solvation and bulky phenyl groups of **1b**. Thus, the single crystal of **1b** has an ideal 1D electronic structure with large bandwidths in both HOMO and LUMO, which might lead to ambipolar field-effect transistor (FET) properties.[16] The large bandwidths are ascribed to the short π–π distance (due to the singlet biradical electronic structure) and efficient HOMO–HOMO and LUMO–LUMO ovarlap (due to a π-overlap arrangement similar to the SOMO–SOMO overlap of the phenalenyl radical dimer).

Solid **1b** gave an extraordinary lower energy shift in the optical spectrum compared to the solution spectrum (Figure 5). The optical conductivity spectra were obtained by Kramers–Kronig transformation of the reflection spectra. Polarization of light along the stacking direction (*b* axis) on the (001) face gave an intense peak at 6804 cm^{-1} ($f=1.9$), whereas no distinct conductivity was recognized below 13000 cm^{-1} along the *a* axis. The oscillator strength along the *b* axis is almost three times larger than that of the intense

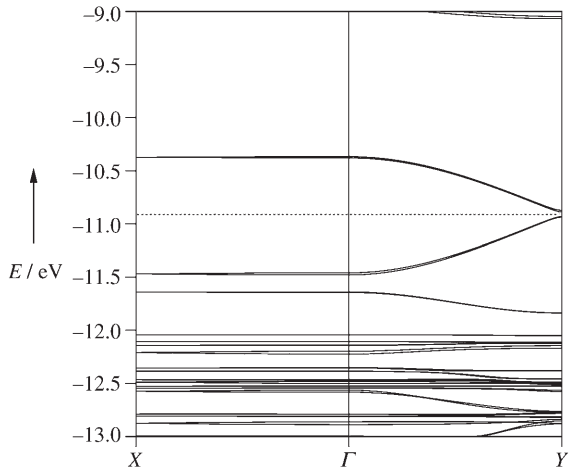


Figure 4. Band structure of **1b** near the Fermi level along *X* (1/2,0,0) and *Y* (0,1/2,0). The dotted line represents the Fermi level.

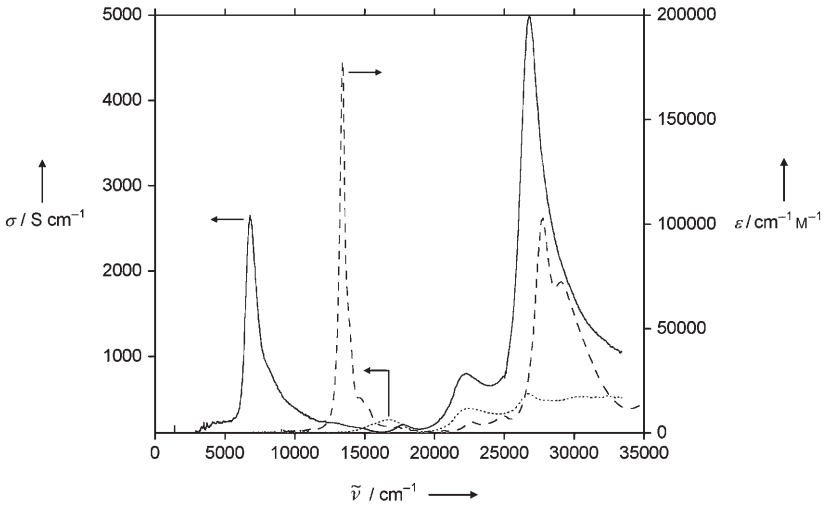


Figure 5. Optical spectra of **1b**. Absorption spectrum in CH_2Cl_2 (-----) and optical conductivities obtained with light polarized along the *a* (•••••) and *b* axes (——).

absorption at 746 nm (13400 cm^{-1}) in solution; that is, the intense band at 6804 cm^{-1} is derived from the lower energy shift of the HOMO–LUMO transition of the monomer due to the intermolecular interactions. The *J*-type stacking of the 1D chain of **1b** seems to imply that the traditional transition dipole–dipole interaction (exciton resonance) is responsible for the lower energy shift. At short intermolecular distances, however, an electron-exchange interaction (charge resonance, i.e., intermolecular HOMO–LUMO transition) becomes important for intermolecular interactions.[17] Of course, the exchange mechanism requires adequate orbital overlap. The orbital overlap between the HOMO and LUMO of solid **1b** is almost identical to the SOMO–SOMO overlap of the phenalenyl radical dimer, and consequently a large overlap integral is expected. Thus, the origin of the lower energy shift should be the configuration interaction between the exciton resonance and the charge resonance states.

Finally, we describe thermal excitation to a triplet state of **1b**. The weak intramolecular coupling between two unpaired electrons leads to a decreased singlet–triplet energy gap ($\Delta E_{S\text{-}T}$). The ^{1}H NMR spectrum of **1b** exhibited severe line broadening of ring protons except for those of phenyl groups at room temperature. On cooling, progressive line sharpening was observed (see Supporting Information). Similar results have been obtained for a tetra-*tert*-butyl derivative of **1a**, which had a $\Delta E_{S\text{-}T}$ value of 20.4 kJ mol^{-1} based on solid-state ESR measurements.[18] Equilibrium with the thermally accessible triplet state would cause line broadening of the NMR signals for **1b**. Magnetic measurements on **1b** showed a gradual increase of χT values above 200 K (see Supporting Information). Using the Bleaney–Bowers equation[19] in the singlet–triplet model gave an estimated $\Delta E_{S\text{-}T}$ value of 2200 K (18 kJ mol^{-1}), which is in good agreement with the result of the ESR measurement.

In conclusion, we have successfully isolated and characterized a biradicaloid hydrocarbon with moderate singlet biradical character. In contrast to most closed-shell compounds, the singlet biradical compound shows strong inter- and intramolecular interactions between two unpaired electrons. Such intermolecular covalency causes substantially close π–π contact, and consequently wide valence and conduction bands are established. Thus, phenalenyl-based singlet biradicals will open up a new avenue for highly delocalized 1D electronic structures.

Experimental Section

The detailed synthetic procedure for **1b** is described in the Supporting Information.

Crystal data for **1b**: $C_{56}H_{34}Cl_2$, $M_r = 777.73$, monoclinic, space group $P2_1/a$ (no. 14), $a = 16.382(14)$, $b = 9.869(8)$, $c = 24.09(2)$ Å, $\beta = 97.065(2)°$, $V = 3865(5)$ Å^3, $Z = 4$, $\mu(Mo_{K\alpha}) = 0.209$ cm^{-1}, $\rho_{calcd} = 1.337$ g cm^{-3}, $R1(wR2) = 0.0691$ (0.1868) for 523 parameters and 6604 unique reflections with $I > 2\sigma(I)$, GOF = 1.135. Data were collected on Rigaku/MSC Mercury CCD diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å) at 200 K. The structure was solved by direct methods and refined with full-matrix least-squares techniques (teXsan). CCDC 275077 contains 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.

Received: July 1, 2005
Published online: September 13, 2005

Keywords: charge transfer · conjugation · density functional calculations · radicals · semiconductors

[1] a) J. Kolc, J. Michl, *J. Am. Chem. Soc.* **1973**, *95*, 7391–7401; b) J. Kolc, J. Michl, *J. Am. Chem. Soc.* **1970**, *92*, 4147–4148; c) J. Downing, V. Dvořák, J. Kolc, A. Manzara, J. Michl, *Chem. Phys. Lett.* **1972**, *17*, 70–73.

[2] M. S. Platz in *Diradicals* (Ed.: W. T. Borden), Wiley, New York, **1982**, pp. 195–258.

[3] L. K. Montgomery, J. C. Huffman, E. A. Jurczak, M. P. Grendze, *J. Am. Chem. Soc.* **1986**, *108*, 6004 – 6011, and references therein.
[4] Isolation and characterization of phenalenyl radicals: a) K. Goto, T. Kubo, K. Yamamoto, K. Nakasuji, K. Sato, D. Shiomi, T. Takui, M. Kubota, T. Kobayashi, K. Yakusi, J. Ouyang, *J. Am. Chem. Soc.* **1999**, *121*, 1619 – 1620; b) Y. Morita, T. Ohba, N. Haneda, S. Maki, J. Kawai, K. Hatanaka, K. Sato, D. Shiomi, T. Takui, K. Nakasuji, *J. Am. Chem. Soc.* **2000**, *122*, 4825 – 4826; c) P. A. Koutentis, Y. Chen, Y. Cao, T. P. Best, M. E. Itkis, L. Beer, R. T. Oakley, A. W. Cordes, C. P. Brock, R. C. Haddon, *J. Am. Chem. Soc.* **2001**, *123*, 3864 – 3871; d) Y. Morita, T. Aoki, K. Fukui, S. Nakazawa, K. Tamaki, S. Suzuki, A. Fuyuhiro, K. Yamamoto, K. Sato, D. Shiomi, A. Naito, T. Takui, K. Nakasuji, *Angew. Chem.* **2004**, *116*, 6503 – 6506; *Angew. Chem. Int. Ed.* **2002**, *41*, 1793 – 1796; e) S. Zheng, J. Lan, S. I. Khan, Y. Rubin, *J. Am. Chem. Soc.* **2003**, *125*, 5786 – 5791; for experimental and theoretical magnetic interaction of phenalenyl radical, see: f) K. Fukui, K. Sato, D. Shiomi, T. Takui, K. Itoh, K. Gotoh, T. Kubo, K. Yamamoto, K. Nakasuji, A. Naito, *Synth. Met.* **1999**, *103*, 2257 – 2258; g) K. Fukui, K. Sato, D. Shiomi, T. Takui, K. Itoh, T. Kubo, K. Gotoh, K. Yamamoto, K. Nakasuji, A. Naito, *Mol. Cryst. Liq. Cryst.* **1999**, *334*, 49 – 58; h) Y. Takano, T. Taniguchi, H. Isobe, T. Kubo, Y. Morita, K. Yamamoto, K. Nakasuji, T. Takui, K. Yamaguchi, *J. Am. Chem. Soc.* **2002**, *124*, 11122 – 11130; phenalenyl-based molecular conductors: i) X. Chi, M. E. Itkis, B. O. Patrick, T. M. Barclay, R. W. Reed, R. T. Oakley, A. W. Cordes, R. C. Haddon, *J. Am. Chem. Soc.* **1999**, *121*, 10395 – 10402; j) M. E. Itkis, X. Chi, A. W. Cordes, R. C. Haddon, *Science* **2002**, *296*, 1443 – 1445; k) S. K. Pal, M. E. Itkis, R. W. Reed, R. T. Oakley, A. W. Cordes, F. S. Tham, T. Siegrist, R. C. Haddon, *J. Am. Chem. Soc.* **2004**, *126*, 1478 – 1484.
[5] Recent advances in singlet biradicals: a) D. R. McMasters, J. Wirz, *J. Am. Chem. Soc.* **2001**, *123*, 238 – 246; b) D. Scheschkewitz, H. Amii, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Science* **2002**, *295*, 1880 – 1881; c) D. Herebian, K. E. Wieghardt, F. Neese, *J. Am. Chem. Soc.* **2003**, *125*, 10997 – 11005; d) D. Scheschkewitz, H. Amii, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Angew. Chem.* **2004**, *116*, 595 – 597; *Angew. Chem. Int. Ed.* **2004**, *43*, 585 – 587; e) M. Bendikov, H. M. Duong, K. Starkey, K. N. Houk, E. A. Carter, F. Wudl, *J. Am. Chem. Soc.* **2004**, *126*, 7416 – 7417; f) M. Abe, W. Adam, W. T. Borden, M. Hattori, D. A. Hrovat, M. Nojima, K. Nozaki, J. Wirz, *J. Am. Chem. Soc.* **2004**, *126*, 574 – 582.
[6] a) K. Nakasuji, T. Kubo, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1791 – 1801, and references therein; b) Short π–π contact due to a singlet biradical electronic structure: T. Kubo, M. Sakamoto, M. Akabane, Y. Fujiwara, K. Yamamoto, M. Akita, K. Inoue, T. Takui, K. Nakasuji, *Angew. Chem.* **2004**, *116*, 6636 – 6641; *Angew. Chem. Int. Ed.* **2004**, *43*, 6474 – 6479.
[7] A referee suggests that the *s*-indacene core should also contribute to the biradical character of **1a** by application of a previously described theoretical consideration: J. R. Dias, *J. Chem. Inf. Comput. Sci.* **2003**, *43*, 1494 – 1501; we thank the referee for this valuable suggestion.
[8] Y. Jung, M. Head-Gordon, *ChemPhysChem* **2003**, *4*, 522 – 525, and references therein.
[9] C. R. Flynn, J. Michl, *J. Am. Chem. Soc.* **1974**, *96*, 3280 – 3288.
[10] Short atom–atom distances: C4–C26 3.088(3), C14–C24 3.101(3), C6–C28 3.160(4), C12–C22 3.104(3), C8–C30 3.167(3), C10–C20 3.121(3), C16–C32 3.224(3) Å; atom-numbering schemes are shown in the Supporting Information.
[11] D. Small, V. Zaitsev, Y. Jung, S. V. Rosokha, M. Head-Gordon, J. K. Kochi, *J. Am. Chem. Soc.* **2004**, *126*, 13850 – 13858.
[12] The RB3LYP/6-31G** calculation on **1a** dimer produces HOMO–HOMO and LUMO–LUMO interactions instead of the HOMO–LUMO interaction which is generally formed in electron donor–acceptor charge-transfer complexes; see Supporting Information.
[13] Hydrocarbon semiconductors: a) H. Inokuchi, N. Matsubara, Y. Maruyama, E. Clar, *Nature* **1965**, *205*, 64; b) Y. Maruyama, H. Inokuchi, Y. Harada, *Bull. Chem. Soc. Jpn.* **1963**, *36*, 1193 – 1198; c) I. Shirotani, H. Inokuchi, S. Minomura, *Bull. Chem. Soc. Jpn.* **1966**, *39*, 386 – 390; see also: M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891 – 4945.
[14] The RHF calculation without CI cannot describe the accurate solid-state electronic structure of singlet biradicals; however, we could not obtain a solution maintaining the singlet biradical character using ab initio programs.
[15] Extended Hückel molecular orbital (EHMO) calculation is known to underestimate HOMO–LUMO energy gaps of molecules, and consequently band structure calculations based on EHT tend to give band gaps smaller than experimental gaps of semiconductors or insulators. In the case of **1b**, the EHMO calculation afforded a HOMO–LUMO gap of 0.511 eV and a band gap of 0.047 eV, which were substantially smaller than the experimentally estimated values.
[16] C. D. Dimitrakopoulos, P. R. L. Malenfant, *Adv. Mater.* **2004**, *16*, 99 – 117.
[17] G. D. Scholes, K. P. Ghiggino, *J. Phys. Chem.* **1994**, *98*, 4580 – 4590.
[18] K. Ohashi, T. Kubo, T. Masui, K. Yamamoto, K. Nakasuji, T. Takui, Y. Kai, I. Murata, *J. Am. Chem. Soc.* **1998**, *120*, 2018 – 2027.
[19] B. Bleaney, K. D. Bowers, *Proc. R. Soc. London Ser. A* **1952**, *214*, 451 – 465.

