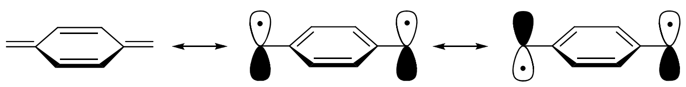
Recent Advances in Kekulé Polycyclic Conjugated Hydrocarbon Biradicals

Bradley D. Rose

Department of Chemistry, University of Oregon, Eugene, Oregon 97403-1253

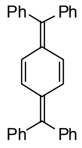
brose@uoregon.edu

ABSTRACT



Kekulé polycyclic conjugated hydrocarbon (KPCH) biradicals lie at the interface of modern theory and experiment. These intriguing species probe the fundamental limits of π-bonding interactions. This critical review focuses on the recent advances that have been made both theoretically and experimentally in relation to KPCH biradicals.

Since their discovery, polycyclic conjugated hydrocarbons (PCH) and their intrinsic properties have fascinated chemists.[1] The idea of PCHs having characteristics of unpaired electrons was kindled with the discovery of organic compounds with unpaired electrons, the first being the triphenylmethyl radical (aka Gomberg's radical) in 1900.[2] Shortly after this Thiele and Tschitschibabin reported their highly reactive hydrocarbons (**1** and **2** respectively) which displayed biradical character.[3] There are two types of PCH-based biradicals, Kekulé polycyclic conjugated hydrocarbon (KPCH) biradicals (e.g., **1**-**2**) and non-Kekulé PCH diradicals. An example of the latter is *m*-xylylene (**3**), which can only be drawn as a diradical. The remainder of the review will use the term biradical to be equivalent to biradicaloid, in order to distinguish from true diradicals such as **3**. This critical review focuses on the fundamentals of the former KPCH biradicals, molecules that push the fundamental limits of π-bonding.[4] The uniqueness of KPCH biradicals comes from the possibility of being represented by several resonance structures. Interestingly, the electronics of KPCH biradicals can be further separated into three viable electronic states–the closed shell singlet (CSS, **4**), the open shell singlet (OSS, **5**), and the triplet (**6**). In contrast diradicals have no closed shell resonance structure.



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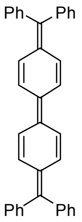

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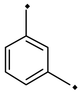

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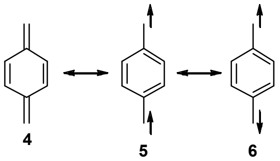

4 **5** **6**

Biradicals typically have high reactivities due to their open shell character, making them difficult to work with, and consequently there are relatively few examples in the literature; however, biradicals have enjoyed lively discussions in the realm of theoreticians.[2,5] Biradicals are not easily represented because of the difficulty in properly describing these systems. Standard self-consistent field (SCF) calculations, such as density functional theory (DFT) and ab initio (e.g., Hartree-Fock), are

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(1) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH, 1997.

(2) Borden, W. T. *Diradicals*; Wiley: New York, 1982.

(3) (a) Montgomery, L. K.; Huffman, J. C.; Jurczak, E. A.; Grendze, M. P. *J. Am. Chem. Soc.* **1986**, *108*, 6004–6011. (b) Thiele, J.; Balhorn, H. *Chem. Ber.* **1904**, *37*, 1463–1470. (c) Tschitschibabin, A. E. *Chem. Ber.* **1907**, *40*, 1810–19.

(4) Sun, Z.; Wu, J. *J. Mater. Chem.* **2012**, *22*, 4151–4160.

(5) Bettinger, H. *Pure Appl. Chem.* **2010**, *82*, 905–915.

fundamentally incapable of accurately describing KPCH systems that possess significant biradical character. The problem lies in the methods themselves. Most closed shell compounds are adequately described by a single wave function (Ψ), or determinant, that is the product of the single electron wavefunctions (ψ_i) (eq 1, Figure 1). In

$$\Psi = \psi_1\psi_2\psi_3 \ldots \qquad (1)$$

biradical systems, however, when two or more of the molecular orbitals are degenerate, or nearly so, this method fails and the electron–electron columbic interaction must be accounted for. One method that can represent biradicals by using static correlation does so by creating a linear combination of several configurations of wavefunctions with a weighing factor (c_i) for each one (eq 2, Figure 1). Generically these calculations that use

$$\Psi = c_1\Psi_1 + c_2\Psi_2 + c_3\Psi_3 + \cdots \qquad (2)$$

multiple configurations are referred to as MCSCF and the minimal treatment for biradicals is called two configuration SCF (TCSCF). Simply put, for KPCH biradicals this latter method is able to include the ground state and a low energy excited state in the final wavefunction (see Figure 1).[2] Notably, this method does not include dynamic electron correlation unless long configuration interaction (CI) expansions are included.[6]

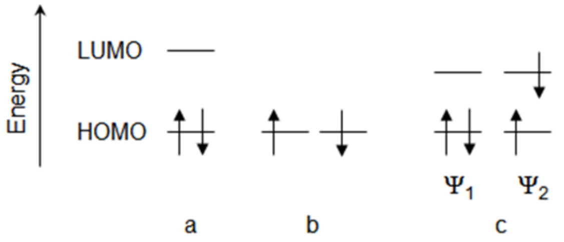

Figure 1. (a) Standard frontier molecular orbitals for a closed shell molecule where all electrons are paired. (b) Idealized biradical with degenerate HOMO and LUMO, or two SOMOs. (c) Example of two wavefunctions that contribute to a TCSCF. For b and c the spin of the electrons was arbitrairly chosen.

More rigorous treatments have also been applied to small systems, CCSD(T) and full CI, but this quickly becomes impractically expensive for larger systems. A practical approach has been utilization of CASSCF(2,2) where the HOMO and LUMO are used for the active space and full CI is performed within this active space. Although less rigorous, unrestricted wavefunctions, such as UHF, have been used with reasonable success for describing biradicals.[7] Broken symmetry (BS) DFT has also offered reasonable results that can be obtained inexpensively. This method accounts for the biradical character by allowing the HOMO and LUMO to mix.[8]

There are several experimental techniques to assess the biradical character and some of the more common ones will be briefly discussed below. KPCHs that have significant biradical character necessarily have a small HOMO–LUMO gap.[9] This gap can be determined from UV/Vis spectrophotometry or electrochemistry. In general KPCHs with noticeable amounts of biradical character have been found to possess a band gap of about 1.5 eV or less. A qualitative way to discern the biradical character is from the ^{1}H NMR spectrum. In KPCHs with ample biradical character, such as **11**, the protons of the core arene are not visible in the NMR spectrum at room temperature due to broadening of the peaks![9] Alternatively, some KPCHs require elevated temperatures for the peaks to broaden. The peak broadening is attributable to a thermally accessible triplet state, which is good indication of a biradical. Raman spectroscopy has also been used to characterize the relative ratio of singlet and triplet species and additionally to extract the singlet-triplet energy difference with the assistance of computations.[11]

KPCH biradicals have largely remained a nebulous concept left in the domain of the theorist. Recently a scheme was developed to experimentally determine a quantitative measure of the biradical character of KPCHs.[7] The experimentally determined biradical character (y_{expt}) was defined as a function of three empirical parameters (eq 3). $^1E_{1u}$ is the lowest energy singlet transition from the one-photon absorption spectrum, $^1E_{2g}$ is the lowest energy transition from the two-photon absorption spectrum and $^3E_{1u}$ is the singlet–triplet energy gap that can be obtained from either phosphorescence or EPR spectroscopy. In this model a perfect biradical would have a value of y = 1 and a closed shell molecule would have a value of y = 0. The

$$y_{\mathrm{expt}} = 1 - \sqrt{1 - \left(\frac{{}^1E_{1u} - {}^3E_{1u}}{{}^1E_{2g}}\right)^2} \qquad (3)$$

experimental y values have been compared to calculated results (y_{calc}) using natural orbital occupation number (NOON) analysis (eq 4) where σ is the NOON for either the HOMO or LUMO.

$$y_{\mathrm{calc}} = 1 - \frac{4(\sigma_{\mathrm{HOMO}} - \sigma_{\mathrm{LUMO}})}{4 + (\sigma_{\mathrm{HOMO}} - \sigma_{\mathrm{LUMO}})^2} \qquad (4)$$

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(6) Neese, F. *J. Phys. Chem. Solids* **2004**, *65*, 781–785.

(7) Kamada, K.; Ohta, K.; Shimizu, A.; Kubo, T.; Kishi, R.; Takahashi, H.; Botek, E.; Champagne, B.; Nakano, M. *J. Phys. Chem. Lett.* **2010**, *1*, 937–940.

(8) Gao, X.; Hodgson, J. L.; Jiang, D.; Zhang, S. B.; Nagase, S.; Miller, G. P.; Chen, Z. *Org. Lett.* **2011**, *13*, 3316–3319.

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(10) Sun, Z.; Huang, K.-W.; Wu, J. *J. Am. Chem. Soc.* **2011**, *133*, 11896–11899.

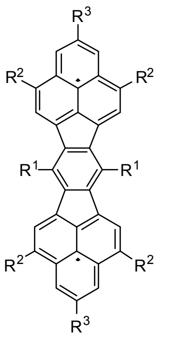
(11) Casado, J.; Patchkovskii, S.; Zgierski, M. Z.; Hermosilla, L.; Sieiro, C.; Moreno Oliva, M.; López Navarrete, J. T. *Angew. Chem. Int. Ed.* **2008**, *47*, 1443–1446.

When compared to computational (UHF) results, the y values obtained from the two methods were found to be very different, but with an approximate linear correlation–y_{expt} were about half the y_{calc} values. More recently the biradical character of these KPCHs was computed using semi–empirical CI methods in an attempt to easily calculate values in better agreement with experiment (Table 1).[12] The withstanding discrepancy between experimental and computed y values leaves room for improvement.

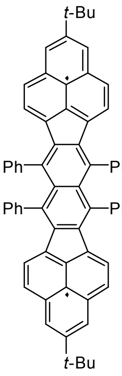
Table 1. Experimentally Determined and Computed Biradical Character (y).

compound	experiment[a]	UHF[b]	semiemperical CI[c]
naphthalene	0.02	0.05	0.01–0.05
anthracene	0.06	0.15	0.06–0.13
chrysene	0.04	0.08	0.02–0.08
fluorene	0.04	0.03	0.00–0.04
7a	0.34	0.76	0.43–0.57
8	0.43	0.86	0.39–0.62
9	0.15	0.45	0.23–0.37

[a] Values from ref 7. [b] Determined using NOONs from UHF/6-31G//UB3LYP/6-31G(d,p); see ref 7 (d) Range of values obtained from semiemperical CI methods used; see ref 12.



7a R^1 = H, R^2 = *t*-Bu, R^3 = H
7b R^1 = Ph, R^2 = H, R^3 = H
7c R^1 = Ph, R^2 = H, R^3 = Me



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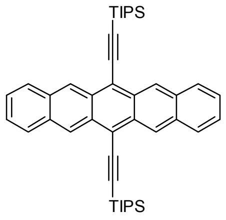

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One class of KPCHs that have been successfully synthesized incorporates phenalenyl motifs. On its own the phenalenyl radical is a non-Kekulé PCH; however, it has cleverly been included in systems such as **7**, **8**, and **10** and **10'**, where closed shell Kekulé resonance structures can be drawn (e.g., **10a'**).[13] The smallest has a benzene linking the phenalenyls (**7a-c**), and these were calculated to have about 34% biradical character.[14] Exclusion of the bulky *t*-butyl group in **7a** yielded suitable crystals of **7b** and **7c**, where the X-ray data, showed overlap of the phenalenyl moiety and sub Van der Walls π–π contacts (3.14–3.28 Å). This unusually close interaction is due to the strongly interacting unpaired electrons. The X-ray data were very interesting as they called attention to the nature of the bonding between the unpaired electrons—was there an *intra*molecular or *inter*molecular bond present? Altering the temperature during data collection or crystallization conditions revealed that it is possible to favor either the intramolecular or intermolecular bonding (Figure 2).[14]

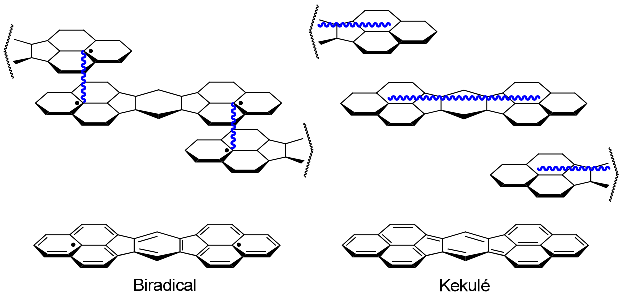
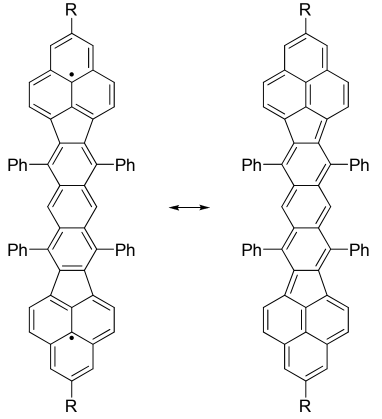


Figure 2. Representation of crystals of **7b** and **7c**; structural details omitted for clarity. Intermolecular electron coupling is larger than intramolecular coupling, indicating more biradical character (left). Intramolecular electron coupling is stronger than intermolecular coupling, thus favoring the Kelulé model (right). Bonding interaction is highlighted in blue.

Expanding **7a-c** with a naphthalene linker (**8**) increased the computed biradical character to 43%. With the enhanced biradical character one would expect the X-ray data to show a larger intramolecular bonding interaction of the biradicals, resulting in closer π-π distances; however, an unencumbered derivative suitable for X-ray analysis has not yet been synthesized. Very recently phenalenyls linked by a fused anthracene have been synthesized (**10a-b**).[13b] DFT calculations indicate that there should be 68% biradical character, keeping in mind that y_{calc} values for DFT have not been compared to y_{exp}. The X-ray crystal structure of **10a** shows strong intramolecular interaction with intramolecular C–C distances of 3.10–3.21 Å for the overlapping phenalenyl moieties, slightly shorter than was found for **7b** and **7c**.



10a R = H
10b R = *t*-Bu

10a' R = H
10b' R = *t*-Bu

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(12) Dral, P. O.; Clark, T. *J. Phys. Chem. A* **2011**, *115*, 11303–11312.

(13) (a) Nakasuji, K.; Kubo, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1791–1801. (b) Shimizu, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T.; Uruichi, M.; Yakushi, K. *Chem. Commun.* **2012**, *48*, 5629–5631.

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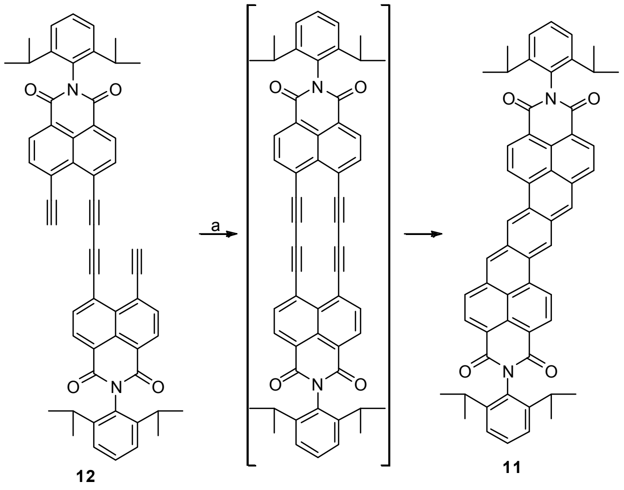
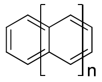
Recently a stable heptazethrene biradical (**11**, shown as its closed shell forn in Scheme 1) was isolated as a result of two spontaneous transannular cyclizations after coupling the terminal ethynyl groups of **12**.[10] This system features carboximide-fused phenalenyls that help lower the energy of the LUMO, thus increasing biradical character. Although the percent biradical character for **11** was not determined, BS-B3LYP calculations predict the OSS to be 5.8 kcal mol^{-1} below the CSS with a spin expectation squared value of 1.017, a near ideal value for an OSS. The triplet state was also computed to be only 7.5 kcal mol^{-1} above the OSS. This is in qualitative agreement with the ^{1}H NMR spectrum, which does not show peaks for the zethrene core until the sample is cooled below ca. –20 °C.

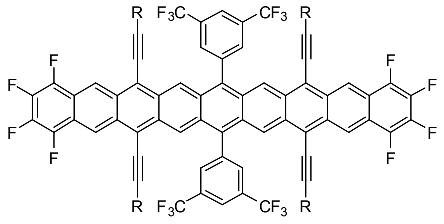
Scheme 1. Synthesis of **11**.



a) Pd(PPh$_3$)$_2$Cl$_2$, CuI, toluene, rt, 1 h. 22% for 2 steps.

Another class of KPCH compounds that have been of great interest are acenes, due to their potential use in electronic devices. One of the most widely studied acenes has been pentacene (n=4), similar to **9**.[14] Acenes can be viewed as discrete linear fragments of graphene whose electronic properties can be studied and systematically manipulated. The smallest acene, benzene (n=0), has a CSS ground state, but as n increases it has been debated as to whether the ground state will be a triplet, OSS, or polyradical.[5] The majority of theory work prior to 2002 favored longer acenes that have a small or non-existent band gap and a Peierls distortion that results in alternating bond lengths. However, newer computational work favors OSS polyradicals, also known as antiferromagnetic polyradicals. The highest acene that has been synthesized to date, nonacene (n=8), was found to have a OSS ground state when photochemically generated, supporting the antiferromagnetic ground state hypothesis.[15] Recently substituted nonacene **13** was isolated and its X-ray data showed no bond length alternation; again supporting the antiferromagnetic ground state.[16]





13a R = Si(*i*-Pr)$_3$
13b R = Si(*i*-Bu)$_3$
13c R = Si(cyclopentyl)$_3$

Graphene–like fragments such as teranthene **14** have been prepared (Figure 3).[17] The driving force for formation of the biradical **14'**, as with 7**a-c**, **8**, **10a-b**, and **11**, is maximizing the number of Clar sextets; **14** has three and **14'** has six. CASSCF(2,2) calculations found the σ_{LUMO} to be 0.42 (or y_{calc} = 0.13 when using eq 2). The very small $^3E_{1u}$ value of 3.82 kcal mol^{-1} indicates that the electrons are very weakly coupled when compared to the other systems discussed.

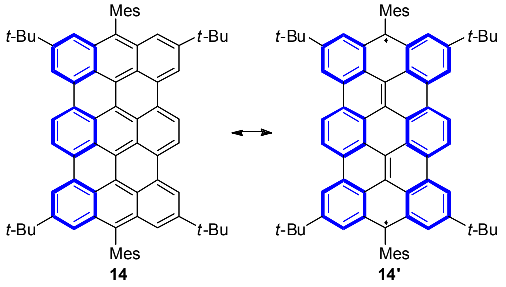


Figure 3. Teranthene shown with Clar sextets hilighted (blue).

The above examples show that exploration of KPCH biradicals is still in its infancy due to the few compounds that are well characterized. While considerable progress has been made in the last decade there still is need for preparation of many additional molecules with rigorous characterization if there is to be a better understanding of the bonding in KPCH biradicals. However, the challenge to close the rift between theory and experiment, while shrinking slowly, still remains. I can only dream about the advances that will happen over the next few decades in the understanding of KPCH biradicals as many more examples of these fascinating molecules are discovered.

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(15) Toenshoff, C.; Bettinger, H. F. *Angew. Chem. Int. Ed.* **2010**, *49*, 4125–4128.

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