Clar Theory for Radical Benzenoids

Anirban Misra,*,[†,‡] T. G. Schmalz,[†] and D. J. Klein[†]

Texas A&M University at Galveston, MARS, 5007 Avenue U, Galveston, Texas 77551 and Department of
Chemistry, University of North Bengal, Darjeeling, PIN 734 013, West Bengal, India

Eric Clar's ideas concerning "aromatic sextets" are extended from closed-shell benzenoids to the case of
radical benzenoids, particularly those where the unpaired electrons are largely localized on sites of one
"type" (starred or unstarred). A quantitative format in terms of a new Clar polynomial is introduced to
make quantitative correlations with a selection of numerical data, including delocalization energies, spin
densities, and energy gaps between states of different spin multiplicities. The correlations are generally
quite good, thereby further validating Clar's ideas and our extension and quantification of them.

INTRODUCTION

About a half century ago Clar proposed his novel theory
of (stable) benzenoids in terms of "aromatic sextets",
describing this theory in a qualitative format, charmingly
illustrated in his short book.[1] The success of his theory
naturally suggested further study, with, e.g., a recent
qualitative discussion being found in Randic's review[2] of
aromaticity. However, rather amazingly few quantifica-
tions with comparisons to chemical data were made in
the three decades following. A general quantification was
made and tested on several types of data in our recent
article,[3] where we also indicate other earlier work toward
quantification. The success of this quantification motivates
further investigation beyond the case of stable (closed-
shell) benzenoids considered there.

Here then these quantified Clar-theoretic ideas are
extended to benzenoid radicals. This is done making some
parallel with classical chemical ideas filtered through the
resonance-theoretic ideas of Pauling[4] and Wheland.[5] That
is, the current theory is phrased in terms of extended Clar
structures, which in addition to identifying aromatic sextets
and lone electron pairings also allow solitary unpaired
electrons. Since the energetic cost of unpairing is severe,
we investigate here circumstances where the extent of
pairing (either in an aromatic sextet or in a lone pairing)
is reasonably restricted to be a maximum. For the
particular class of radical molecules we presently consider,
the number of unpaired electrons arising in these Clar
structures is simply the difference between the numbers
of starred and unstarred sites, where these two types of
sites are chosen such that every site of one type has
neighbors solely of the other type. (Our extended Clar
structures are in fact also indicated by Clar, in XII, XXXI,
and XXXII, of chapter 23 of his book, so that one could
plausibly even leave off the adjective "extended".) As an
example of such a Clar structure *C*, consider the peri-
naphthyl radical as indicated in Figure 1. In addition to
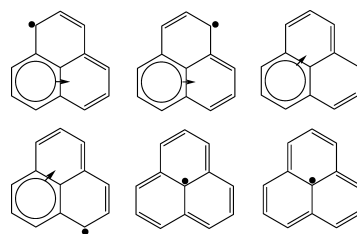
Figure 1. Extended Clar structures of the peri-naphthyl radical.

the 4 extended structures in the first row of this figure,
there are two similar sets of 4 others with the aromatic
sextet appearing in either of the two other hexagonal rings.
The arrows indicate that the sextet can migrate to the other
positions indicated with rearrangement only of the bonding
pattern in the two rings so interconnected. The two
structures *C* appearing in the second row lack a Clar sextet
and hence are anticipated to be of lesser importance, as
is encoded in an extended Clar 2-nomial, which for the
case of peri-naphthyl is $12xy + 2$. That is, this (extended)
Clar 2-nomial is a sum over all extended Clar structures
C of a benzenoid *B* with a weight w_C, which is a power
of nominal variables, *x* and *y*, the power of *x* counting
the number of aromatic sextets in *C* and the power of *y*
counting the number of arrows in *C* to indicate the
migratory ability of the sextets. This is in close parallel
with our earlier quantification,[3] which otherwise did not
envisage the possibility of unpaired electrons. In this work
total 18 (I−XVIII) different benzenoid radicals have been
investigated for different properties like delocalization
energy, spin density, and spin multiplet splitting, which
are shown in Figure 2. Clar 2-nomials for all 18 species
are given in Table 1.

Now with the possibility of unpaired electrons in a Clar
structure, one may consider an unpaired-electron counter
$u_i(C)$ which is 1 or 0 as an unpaired electron either appears
or does not appear on site *i* in Clar structure *C*. Hence, a
Clar free valence for a site *i* in a benzenoid *B* naturally arises
as

* Corresponding author phone: +919434228745; fax: +913532581212;
e-mail: anirbanmisra@yahoo.com.
  [†] Texas A&M University at Galveston.
  [‡] University of North Bengal.

CLAR THEORY FOR RADICAL BENZENOIDS

J. Chem. Inf. Model., Vol. 49, No. 12, 2009 **2671**

$$CFV_B(i) = \sum_C w_C \cdot u_i(C)/C_B(x,y) \qquad (1)$$

with w_C being the weight for C and $C_B(x,y)$ the (extended) Clar 2-nomial. That is, this is just the mean number of times an unpaired electron ends up on site i (with the Clar structures weighted as indicated.) The bond-order and ring-aromaticity indices remain as before.[3] Hence, for peri-naphthyl one obtains free valences of $2xy/(12xy + 2)$ at the set of 6 alternating degree-2 positions meta to the central site, for which the free valence is $2/(12xy + 2)$: the remaining sites ortho and para to the center site have 0 free valence. With our earlier canonical choice for x and y (namely, $x = 2$ and $y = 1$) these respective values are 2/13 and 1/13. Notably in this case this result is exactly the same as for an ordinary resonance-theoretic definition of Pauling free valence taken as 1 minus the sum of the Pauling bond orders incident at a
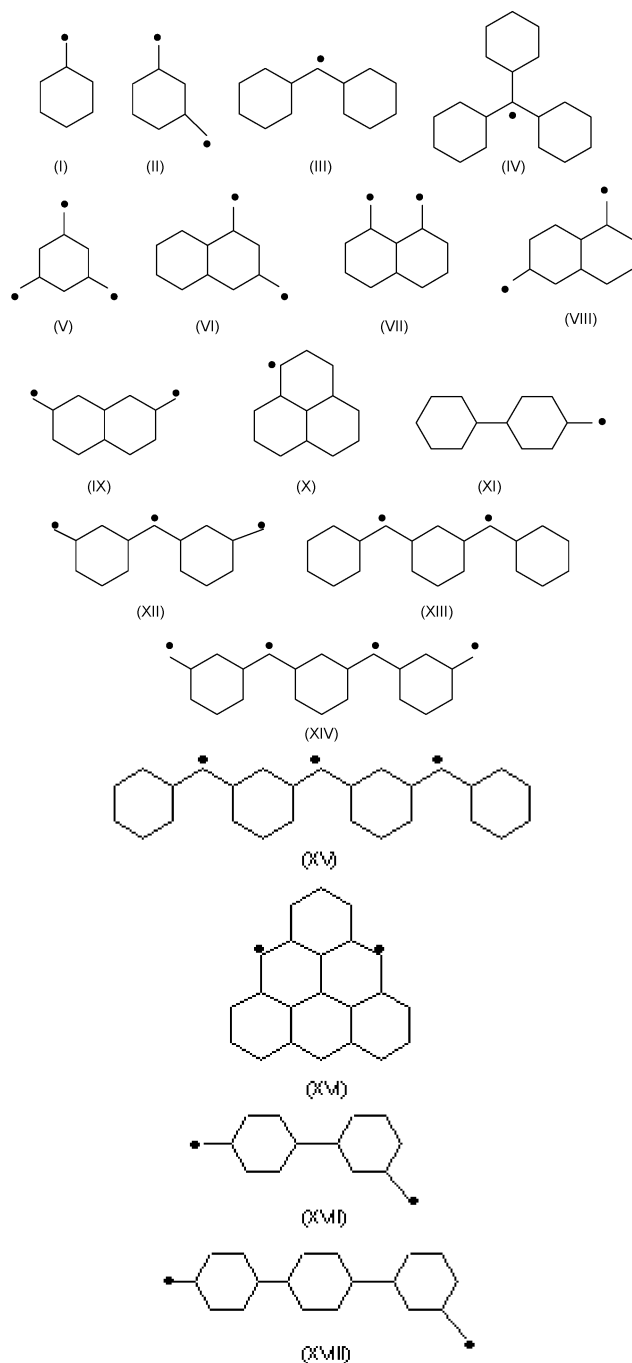
Table 1. Clar 2-Nomials for Benzenoid Radicals Given in Figure 2

species	Clar 2-nomial
I	$x + 3$
II	$x + 8$
III	$x^2 + 6x$
IV	$x^3 + 9x^2$
V	$x + 16$
VI	$2xy + 4x + 10$
VII	$2xy + 4x + 14$
VIII	$2xy + 3x + 15$
IX	$2xy + 2x + 15$
X	$12xy + 2$
XI	$x^2 + 3x + 3$
XII	$x^2 + 16x + 39$
XIII	$x^3 + 114x^2 + 27x$
XIV	$x^3 + 25x^2 + 142x + 162$
XV	$x^4 + 22x^3 + 114x^2 + 108x$
XVI	$18x^2y^2 + 27x^2y + 24x^2 + 93xy^2 + 240xy + 18x + 108$
XVII	$x^2 + 6x + 14$
XVIII	$x^3 + 6x^2 + 12x + 14$

site. Generally, the free valence of Clar is similarly related to Clar bond orders

$$CFV_B(i) = 1 - \sum_e^{@i} CBO_B(e) \qquad (2)$$

where the sum is over edges incident to site i. In cases other than peri-naphthyl the Clar and Pauling free valences can differ from one another (inasmuch as the Clar and Pauling bond orders have already been noted[3] to differ).

With such extensions of our quantifications earlier applied to nonradicaloid benzenoids, correlations to several relevant types of chemical data are sought. In particular, we treat delocalization energies, spin densities, and splittings between the high-spin ground state and excited states of lower spin for a set of representative benzenoid radicals. Further properties earlier treated[3] for the nonradical species included bond lengths and NICS local aromaticity indices, which typically however have been less a focus of interest for radical species and so are not currently considered. The properties here focus on the unpaired electrons, which are crucial in accounting for magnetic properties and ultimately electrical conduction in larger nanostrucutures.

CORRELATIONS TO DELOCALIZATION ENERGIES

We treat a representative collection of benzenoid radicals, I–XVI, as indicated in Figure 2. One systematic means by which to compute π-electron energies is the all-covalent-structure Pauling–Wheland VB model, and this we do using a full-CI scheme[6] which is feasible up to ∼30 sites. This model is also known as the isotropic spin-1/2 Heisenberg model, and for a benzenoid B may be written as $H_{VB} = J\sum_{ij}^B 2\vec{s}_i \cdot \vec{s}_j$ with J being the exchange parameter. Delocalization energies VBDLE(B) are defined as the difference between the computed energy and the energy of a number of ethylenes equal to the number of pairs in a typical Kekule structure. We then seek a correlation of this VBDLE to a Clar delocalization energy

$$CDLE(B) = A_1\langle s\rangle_B + A_2\langle a\rangle_B + A_3 \cdot u_B \qquad (3)$$

where A_1, A_2, and A_3 are parameters, u_B is the number of unpaired electrons, $\langle s\rangle_B$ is the mean sextet count, and $\langle a\rangle_B$ is the mean arrow count. (The notation for these two means

Figure 2. Set of benzenoid radicals used in this study.
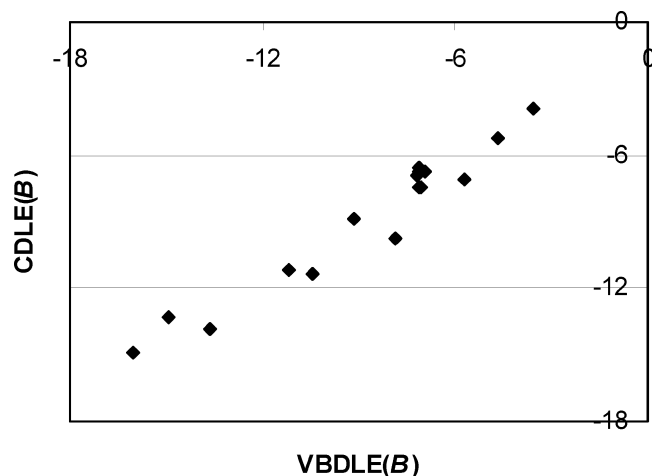
Figure 3. Plot of Clar delocalization energy vs valence bond delocalization energy for the benzenoids (I−XVI in Figure 2). Both are in units of Joules.

and their use is described in our earlier work.[3]) A least-squares fit of the parameters yields

$$A_1 = -4.181J, \ A_2 = -4.044J, \ A_3 = -2.203J \quad (4)$$
$$\sigma = 0.299, \ r = 0.973$$

where σ is the root mean squared deviation between the VBDLE and CDLE values and r is the correlation coefficient. A detailed comparison is made in Figure 3. Evidently the fit is quite reasonable. The success here might be anticipated from, first, an earlier good fit[7] to (signed) counts of Kekule structures for resonance energies of various radical species and, second, the close relation between our Clar-theoretic approach and such Paulingesque[4] counting schemes. Here we wish to test whether further information is implicit in our Clar-theoretic treatment, e.g., concerning spin densities and low-lying excitations. Notably the computation involved in our Clar-theoretic approach is much less than that for full-CI computations on the Heisenberg model. Hence, the current approach might be more readily applicable to large nano-structural systems.

CORRELATIONS TO SPIN DENSITIES

Here also a representative collection of benzenoid radicals (I−X of Figure 2) is treated to make comparisons to quantum-chemically calculated spin densities. Three different quantum-chemical schemes for spin densities are entertained: first, full-CI Heisenberg-model computations, second, UHF computations on the Hubbard model, and, third, density functional computations at the UB3LYP level. Here the spin density computed is the difference in electron densities of α- and β-spin electron densities and typically turns out to be positive on some sites while it is negative on other sites. The pattern of signs is generally viewed[8] to manifest "spin polarization" wherein a spin density on a site induces a counter-signed spin density on neighboring sites. The Clar free-valence index is nominally an unpaired electron density, which for our current species has nonzero values confined to sites of one type with 0 values on the sites of the other types. Hence, to account for spin polarization, we consider a Clar spin-polarization index which sums up the values of the free valence at neighboring sites

$$CSP_B(i) \equiv \sum_{j}^{\sim i} CFV_B(j) \quad (5)$$

which up to proportionality is assumed to give the counter-signed spin density at the minority sites (here taken as "unstarred"). That is the spin density is to be proportional to $+CFV_B$ at starred sites and $-CSP_B$ at unstarred sites. Moreover, this proportionality is scaled so that the sum of all the spin densities retains its proper sum, namely, $2S_B$, where S_B is the ground-state spin of B (which in our case is just the number of starred sites minus the number of unstarred sites and interpreted as the net number of unpaired electrons appearing in our extended Clar structures). That is, the Clar spin density is given as

$$CSD_B(i) = \begin{cases} CFV_B(i) \cdot 2S_B / \{2S_B - C \cdot SP_B\}, i \text{ starred} \\ -C \cdot CSP_B(i) \cdot 2S_B / \{2S_B - C \cdot SP_B\}, i \text{ unstarred} \end{cases} \quad (6)$$

where C is a parameter (measuring the "strength" of the spin polarization) and SP_B is the sum over all the spin polarization terms, namely, $SP_B \equiv \sum_i^B CSP_B(i)$.

Fits of C for our Clar spin density have been made to the spin density ρ computed via three different computational methods. Here CSD is nonlinear in the parameter C, but we can apply ordinary linear least-squares fitting if we fit $\{2S_B - C \cdot SP_B\}\rho_B(i)$ against $CFV_B(i) \cdot 2S_B$ or $-C \cdot CSP_B(i) \cdot 2S_B$ as the site i is starred or unstarred. First, we made exact solutions for the Heisenberg model using computational methodology elsewhere described[6] and carried out a fitting

$$C = 0.282 \quad (7)$$
$$\sigma = 0.119, \ r = 0.964$$

Second, we performed UHF solutions for the Hubbard model (with $|U/t| = 1.45$) with the resultant fit being

$$C = 0.134 \quad (8)$$
$$\sigma = 0.072, \ r = 0.966$$

Third, we also carried out UB3LYP solutions for the ordinary Schrödinger Hamiltonian using a standard GAUSSIAN 03W package.[9] We take the spin density at a site i of B to be the sum of that of the carbon atom and the smaller amount at any attached H atoms, thereby including all the spin density. The resultant fit is

$$C = 0.198 \quad (9)$$
$$\sigma = 0.076, \ r = 0.975$$

The detailed comparisons for each of these three (1-parameter) fittings are given in Figures 4−6. All three fits are quite good, indicating a substantial degree of accuracy for our simple Clar-theoretic model. The values of C for the different (semiempirical or ab intitio) computational methods are somewhat different as they predict rather different spin densities, which however seem to be largely scaleable into one another. We surmise that the UB3LYP spin densities are the most realistic, which is rather expected.

DIGRESSION ON CONTRACTION OF EXTENDED CLAR STRUCTURES

The extended Clar structures of this paper are typically more numerous than the ordinary Clar structures of compa-rably sized species, so that it becomes of some interest to present an abbreviated or contracted notation for them.
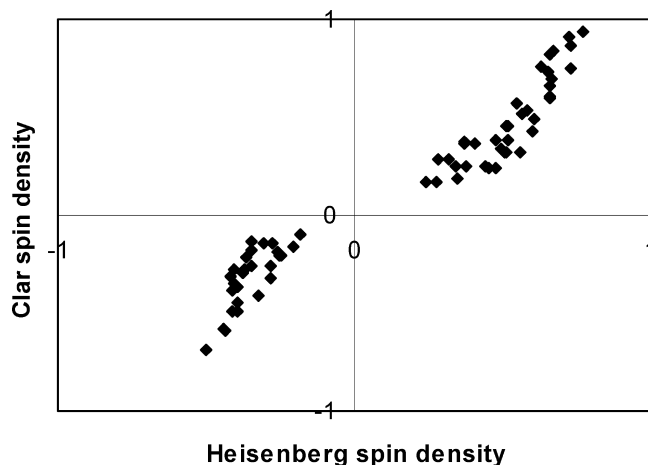
Figure 4. Plot of Clar spin density vs Heisenberg-model spin density.
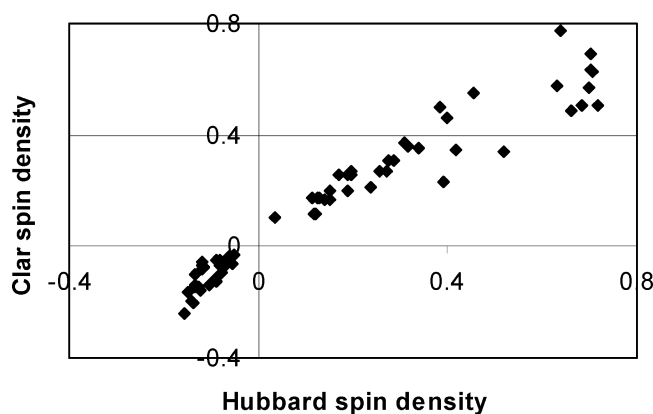

Figure 5. Plot of our Clar spin density vs (UHF) Hubbard-model spin density.
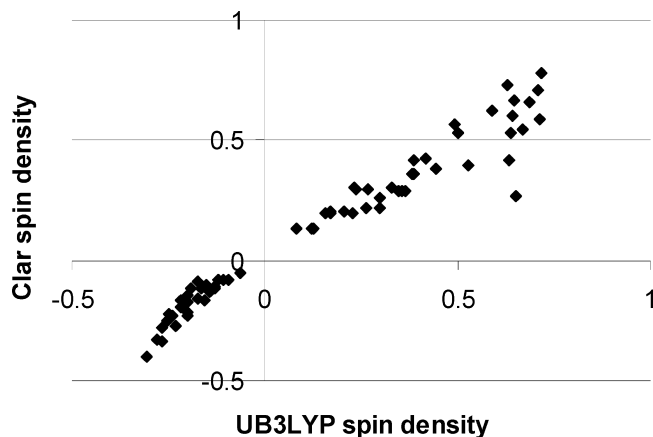
Figure 6. Plot of Clar spin density vs UB3LYP spin density.

Basically with fixed sextet rings one might abbreviate several with unpaired electrons in different locations, e.g., the first four extended Clar structures of Figure 1 might simply be represented in the single contracted representation of Figure 7. There the open circles on the 4 sites represent possible locations for the unpaired electron, while the curve along the set of 7 sites indicates that the remaining 6 sites are to be paired up in isolated pairs.

Such an abbreviation becomes even more useful with even larger structures, so that for the benzenoid diradical of Figure 8, we find just 8 of the contracted structures to represent the species in lieu of the otherwise 33 different extended Clar
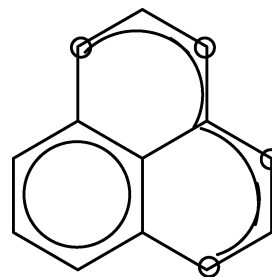
Figure 7. Compact form of the first four Clar structures of the peri-naphthyl radical.

structures. For the next member in this sequence (quatra-phenyl with two methenyl groups attached at the ends in just the same way) one finds 10 contracted structures in lieu of 45 extended Clar structures.

A further point is that this contraction aids in seeing general patterns as arises in sequences of oligomers, so that the Clar 2-nomial for a general *N*-mer may be identified. Such an example is illustrated at the end of the next section.

CORRELATIONS TO SPIN-MULTIPLET SPLITTINGS

Finally, energetic splittings from the high-spin ground state to the lowest energy state of the next lower spin are considered. This precludes our doublet ground-state monoradicals, and it, respectively, corresponds to a triplet−singlet or quartet−doublet splitting for our diradicals or triradicals. This splitting is plausibly imagined to relate to the mutual arrangement of the electrons which are unpaired in the ground state and are to become paired in the excited state. That is, the Clar structures each correspond to different resonance-theoretic contributions to the overall wave function, each structure involving an unpaired electron predominantly in a perpendicularly oriented p_z orbital at a particular site, so that the interaction between two such unpaired electrons should fall off notably and systematically with distance between the two sites. Thus, we introduce a distance-dependent decoration of our extended Clar 2-nomial

$$C_B(x, y, t) \equiv \sum_C^B x^{s(C)} y^{a(B)} \sum_{i,j}^{C-\text{unpaired}} t^{d_{ij}} \qquad (10)$$

Here the *i,j* sum is over pairs of sites with unpaired electrons in the extended Clar structure *C*, *t* is a (dummy) variable, and d_{ij} is the minimum number of bonds traversed between *i* and *j*. Then

$$\langle d_{ij} \rangle_B \equiv \frac{\partial \ln C_B(x, y, t)}{\partial \ln t}$$

$$= \left\{ \sum_C^B x^{s(C)} y^{a(B)} \sum_{i,j}^{C-\text{unpaired}} d_{ij} \cdot t^{d_{ij}} \right\} / C_B(x, y, t)$$

$$(11)$$

gives an average distance between (initially) unpaired sites, and we evaluate at $x = 2$, $y = 1$, and $t = 1$. In as much as the pairing instituted in the excited state should entail a less energetic cost the greater the distance between the initially unpaired sites, we plausibly imagine that the (high-to-low) spin splitting Δ should be inversely related to this distance. Hence, we define a Clar spin splitting as

$$CSS_B = D/\langle d_{ij}\rangle_B^2 \qquad (12)$$

with but a single proportionality parameter D to be fit to the experimental splittings Δ_B.

We compare our Clar spin splitting expression of eq 12 with the experimental spin splittings for the ground-state triplet and quartet radicals of II, V−IX, XII, XIII, XIV, XVII, and XVIII
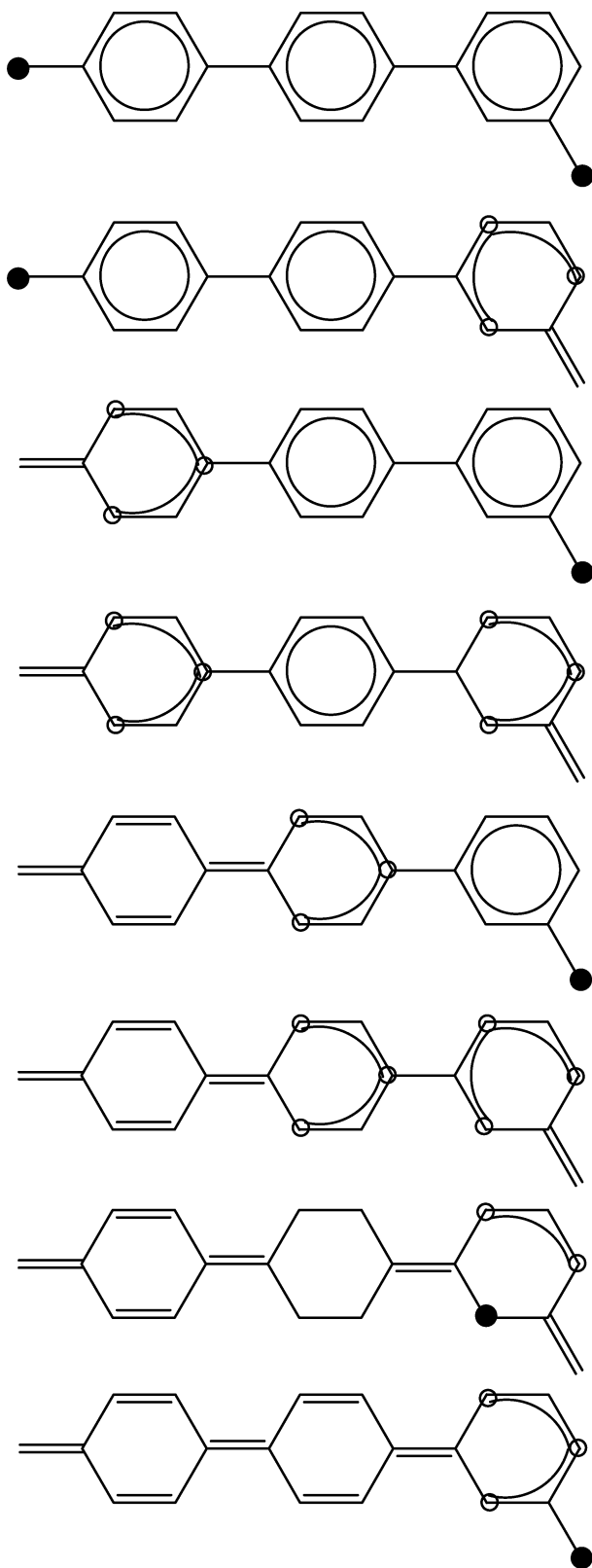
Figure 8. Compact form of the Clar structures for a three ring benzenoid biradical.
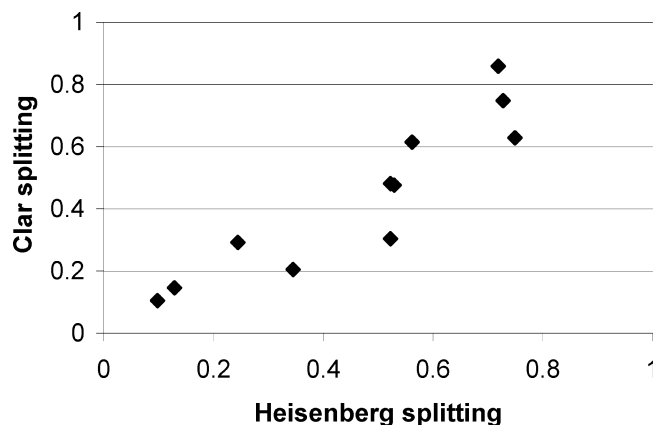
Figure 9. Plot of Clar spin splittings vs Heisenberg-model spin splittings. Energies are in units of Joules.

from Figure 2. The "experimental" Δ_B splitting data to be fit against are obtained from the Pauling−Wheland VB model, again[6] with full CI. A least-squares fitting to this gives

$$D = 6.731\,\mathrm{J} \qquad (13)$$
$$\sigma = 0.101, \quad r = 0.914$$

which seems quite reasonable statistics (for a 1-parameter fit). A plot of the predicted vs "experimental" data is shown in Figure 9. Evidently a reasonable correlation is obtained.

It may be noted that our analysis in terms of Clar structures readily yields predictions for infinite (i.e., polymeric) sequences far beyond what is exactly treatable by ordinary full CI for the Heisenberg spin Hamiltonian. One such case involves the sequence of diradicals $B(N)$ beginning at $N = 1$ for *m*-dimethenyl-benzene and continuing with ever longer poly phenyl (or poly-*p*-phenylene) chains: the $N = 3$ member appearing in Figure 8. The Clar polynomial for a general member of this family may be seen to be

$$C_{B(N)}(x, y, t) = (xt^4)^N + (\alpha + \beta)(xt^4)^{N-1} +$$
$$(\alpha + \alpha\beta)\{(xt^4)^{N-2} + (xt^4)^{N-3} + \dots + $$
$$(xt^4)\} + \beta + \alpha\beta + 2t^2 \qquad (14)$$

where we abbreviate $\alpha \equiv 1 + 2t^2$ and $\beta \equiv 2t^2 + t^4$. This formula applies for all $N \geq 2$, if we understand the "eagle-bracketed" term to reduce to 0 if $N = 2$ (and to just one term if $N = 3$). At $t = 1$ the Clar 2-nomial of the preceding sections is recovered.

To utilize this resultant polynomial to predict splittings for the whole sequence, one needs to take the derivative (with respect to t) of the polynomial in eq 14 then use the values $x = 2$ and $y = 1 = t$ in the expression of eq 11 to obtain

$$\langle d_{ij}\rangle_{B(N)} = \left\{4N - \frac{29}{5} + \frac{32}{5}\cdot 2^{-N}\right\}/\{1 - 2^{-N}\} \qquad (15)$$

Thus, for large N one has

$$CSS_{B(N)} \approx D/\left(4N - \frac{29}{5}\right)^2 \qquad (16)$$

so that the splitting from the ground-state triplet to the lowest excited singlet is predicted to approach 0, inversely with the chain length. Since the exchange parameter is reasonably estimated[6] as $J \cong 1.80$ eV, one sees that the chain needs to become modestly long (of more than a dozen rings) before the splitting becomes small enough that the excited (lower spin) state should be substantially populated at room temperature. Within the context of the Heisenberg model, it is known[10,11]
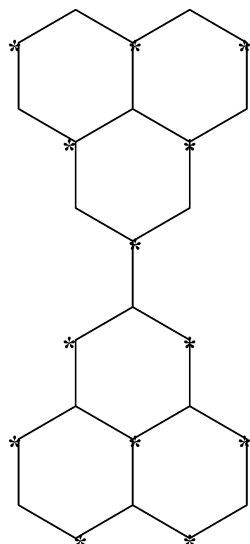
CLAR THEORY FOR RADICAL BENZENOIDS

J. Chem. Inf. Model., Vol. 49, No. 12, 2009 **2675**

Figure 10. Starred and unstarred sites in bis-peri-napthyl species.

(by theorem) that the triplet always remains above the singlet, which then is permanently the ground state.

CONCLUSION

It is seen that Clar's qualitatively illustrated[3] ideas, though harking back to classical chemical bonding ideas in application to stable (closed-shell) benzenoids, evidently extend in a fairly plausible way to quantitatively treat several different molecular properties for a range of benzenoid radicals. The properties tested here include delocalization energies, spin densities, and high- to low-spin-state splittings. Our extensions are intimately related to Pauling−Wheland resonance theory, which however in its simpler (structure-counting) form has been relatively little used to deal with these radical species (though see ref 7). At the same time it has been long realized[10,12−21] that the quantitative all-covalent structure VB model of Pauling and Wheland (which is the same as the Heisenberg model) performs quite reasonably for radicals (at least for alternants without 4-membered rings). The reasonable fits of the Clar results to the Heisenberg values give assurances to the predictions for the much larger species such as those considered briefly near the end of the preceding section and are not treatable via exact solution of this Heisenberg model or perhaps even approximate resonance-theoretically based solutions involving CI among Kekule structures (e.g., as in refs 22−24).

The radicals here have been of a special kind, wherein the neighbor-pairing patterns fully pair the sites of one type (starred or unstarred). There are of course radicals of another class where unpaired electrons occur on sites of both types, one example of this being the bis-peri-naphthyl species of Figure 10, where the maximally paired Clar structures are simply obtained as combinations of those for peri-naphthyl radical moieties on the two ends of this species. These are delayed to a future work as they entail slightly modified considerations, as also seem important in treating electrical conduction in conjugated polymers where singular sites (now with an extra electron or a deficit of a electron) also arise, typically in separated pairs on different types of sites if the polymer otherwise manifests full pairing.

Overall our results recommend our interpretation and quantification of Clar's ideas. In particular, the present definition of extended Clar structures is supported along with our form of Clar polynomial, incorporating "sextetness", "mobility", and "unpairing" ideas in a natural way, notably in consonance with Pauling−Wheland resonance-theoretic ideas. We surmise that similar quantifications should apply for several other properties. However, of key interest for us is the prospect for the application of Clar's theory, as embodied in the new ideas and invariants introduced here, to treat related novel conjugated nanostructures along with further relevant magnetic and electric properties. It is notable that all seems to extend nicely to account for unpaired sites, as is crucial in understanding magnetic properties and electrical conduction. The success registered here is a further step forward in this enterprise to develop simple classical ideas to deal with modern nanostructural questions.

REFERENCES AND NOTES

(1) Clar, E. Robinson's Aromatic Sextet. In *The Aromatic Sextet*, 1st ed.; John Wiley & Sons: New York, 1970; pp 13−16.
(2) Randic, M. Aromaticity of Polycyclic Conjugated Hydrocarbons. *Chem. Rev.* **2003**, *103*, 3449–3606.
(3) Misra, A.; Klein, D. J.; Morikawa, T. Clar Theory for Molecular Benzenoids. *J. Phys. Chem. A* **2008**, *113*, 1151–1158.
(4) Pauling, L. The Resonance of Molecules Among Several Valence-Bond Structures. In *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 198−209.
(5) Wheland, G. W. Mathematical Basis of Resonance. In *Resonance in Organic Chemistry*, 1st ed.;John Wiley & Sons: New York, 1955; pp 544−694.
(6) Alexander, S. A.; Schmalz, T. G. π-Electron Valence Bond Calculations on Benzenoid Hydrocarbons via Graphical Unitary Group Methods. *J. Am. Chem. Soc.* **1987**, *109*, 6933–6937.
(7) Herndon, W. C. Resonance Energies of.pi. Hydrocarbon Radicals. Radical Reactivities of Polycyclic Aromatic Hydrocarbons. *J. Org. Chem.* **1981**, *46*, 2119–2125.
(8) Carrington, A.; MacLachlan, A. D. Spin Distributions in Odd Alternant Radicals. In *Introduction to Magnetic Resonance*, 1st ed.; Harper & Row: New York, 1979; pp 86−91.
(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03 W*; Gaussian, Inc.: Wallingford, CT, 2004).
(10) Ovchinnikov, A. A. Multiplicity of the ground state of large alternant organic molecules with conjugated bonds. *Theor. Chim. Acta* **1978**, *47*, 297–304.
(11) Klein, D. J.; Nelin, C.; Alexander, S.; Matsen, F. A. High-spin hydrocarbons. *J. Chem. Phys.* **1982**, *77*, 3101–3108.
(12) Lefkovits, H. C.; Fain, J.; Matsen, F. A. Complete π-Electron Treatment of Allyl Radical and Allyl Ion. *J. Chem. Phys.* **1955**, *23*, 1690–1692.
(13) McConnell, H. M.; Dearman, H. H. Spin Densities in the Perinaphthenyl Free Radical. *J. Chem. Phys.* **1958**, *28*, 51–53.
(14) Barfield, M. Valence-Bond Calculations of Triplet-State Energies and Spin Densities of Unsaturated Organic Molecules. *J. Chem. Phys.* **1967**, *47*, 3831–3836.
(15) Barfield, M. Valence-Bond Studies of Contact Nuclear Spin-Spin Coupling. I. A Truncated Matrix Sum Method. *J. Chem. Phys.* **1968**, *48*, 4458–4462.

MISRA ET AL.

(16) Hiberty, P. C.; Karafiloglou, P. The Valence Bond Description of Xylylenes. *Theor. Chim. Acta* **1982**, *61*, 171–177.

(17) Koutecky, J.; Dohnert, D.; Wormer, P. E. S.; Paldus, J.; Cizek, J. Spin Properties of Radicaloid Alternant Hydrocarbons. Exact Solutions for Representative Pariser-Parr-Pople Model Systems. *J. Chem. Phys.* **1984**, *80*, 2244–2246.

(18) Klein, D. J.; Alexander, S. A.; Randić, M. Polyradicals and High-Spin Hydrocarbons. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 109–114.

(19) Sinha, B.; Albert, I. D. L.; Ramasesha, S. Stability of the High-Spin Ground State in Alternant π-Conjugated Organic Molecules. *Phys. Rev. B* **1990**, *42*, 9088–9097.

(20) Li, S.; Ma, J.; Jiang, Y. Topological Dependence of Ferromagnetic Coupling Strength in Some π-Conjugated Radicals. *Chem. Phys. Lett.* **1995**, *246*, 221–227.

(21) Ma, J.; Li, S.; Jiang, Y. Can the Low-Lying Electronic States be Described by the Semiempirical Valence Bond Approach? *J. Phys. Chem. A* **1997**, *101*, 4770–4775.

(22) Li, X.; Paldus, J. Valence Bond Approach to the Pariser-Parr-Pople Hamiltonian and its Application to Simple π-Electron Systems. *J. Molec. Struct. (THEOCHEM)* **1991**, *229*, 249–278.

(23) Flocke, N.; Schmalz, T. G.; Klein, D. J. Ground and Excited Hubbard States for Buckminsterfullerene with Uniform and Alternating Bond Strengths. *J. Chem. Phys.* **2000**, *112*, 8233–8240.

(24) Wu, J.; Schmalz, T. G.; Klein, D. J. An Extended Heisenberg Model for Conjugated Hydrocarbons. II. Kekulé Basis. *J. Chem. Phys.* **2003**, *119*, 11011–11016.