JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 8, 103–107 (1995)

ARE KEKULENE, CORONENE, AND CORANNULENE TETRAANION SUPERAROMATIC? THEORETICAL EXAMINATION USING HARDNESS INDICES

ZHONGXIANG ZHOU†

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290, USA

The superaromaticity concept is examined and developed, taking into account what is known about aromaticity. Three new hardness indices are defined, and shown to be excellent parameters for characterizing superaromaticity. High superaromaticity indicates significant global annulenoid conjugation relative to local benzenoid conjugation in circularly annealed benzenoid molecules. Kekulene, coronene and corannulene tetraanion all are predicted to be superaromatic. The prediction for the corannulene tetraanion strongly supports the 'annulene-within-an-annulene' structure derived from NMR data.

The topic of global annulenoid conjugation versus local benzenoid conjugation has been the focus of several recent studies, both theoretical and experimental.[1–3] Theoretically this has been put into the context of superaromaticity. Cioslowski *et al.*[1] calculated the superconjugative energy component for kekulene (see Figure 1) and reached the conclusion that kekulene is slightly superaromatic. Aihara[2] concluded from his careful graph-theoretical examinations of kekulene that superaromaticity is more an artifact than a reality. A recent NMR study of corannulene tetraanion strongly suggested that an 'annulene-within-an-annulene' structure exists for the tetraanion.[3] Approximately one of the four negative charges is distributed among the atoms in the inner ring and three among the outer ring. The macrocyclic conjugation is important in this system. In this paper, we first summarize the common characteristics of aromaticity and superaromaticity and address the difficulties in quantifying superaromaticity. We then examine the concept of superaromaticity by applying three hardness indices, which we introduce, to three molecules: kekulene, coronene and corannulene tetraanion (see Figure 1). The three hardness indices differ from each other in the way in which their reference hardnesses are defined [see equaitons (1), (2) and (3)]. We show that the superconjugation effect (annulenoid conjugation) is not a negligible effect, at least for corannulene tetraanion.

Aromaticity arises from cyclic conjugation. Any property associated with the cyclic conjugation of aromatic molecules can be used as an indicator of aromaticity (see, e.g. Ref. 4). Superaromaticity is the part of the aromaticity that is associated with the macrocyclic conjugation of circular benzenoid rings.[12] Superaromatic molecules are benzenoid molecules annealed in such a way that all benzene units form a macrocyclic system.

Over the years, many successful indices for aromaticity have been introduced. Some are based on valence bond theory.[5–10] Others are based on molecular orbital theory.[11,12] Although there are some flawed doubts towards the π-electron-only indices for aromaticity in the literature[13,14] these indices seem to give predictions consistent with experimental facts and with each other. There is something in common among all the aromaticity indices, that is, that contributions from acyclic components are to be taken away. How successful this can be done determines how successful an aromatic index is. Early aromatic indices using polyene or ethene as reference structures were not successful because these reference structures could not lead to the correct acyclic contributions to physico-chemical properties of aromatic molecules. The recent successful definitions of aromaticity involved reasonable definitions of reference structures.[5–12]

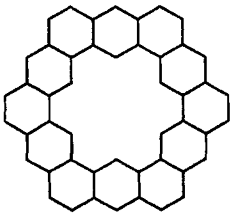
Investigation of superaromaticity started with McWeeny's suggestion[15] that kekulene should provide a crucial test for different predictions of the diamagnetic anisotropy of aromatic systems from Pauling's semi-empirical method[16] and from molecular orbital

---

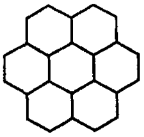
[*] Present address; Protein Design Laboratories, Inc., 2375 Garcia Avenue, Mountain View, CA 94043, USA.

CCC 0894-3230/95/020103-05

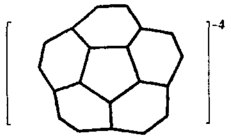
Received 21 June 1994



Kekulene



Coronene



Corannulene tetraanion

Figure 1. Kekulene, coronene and corannulene tetraanion

calculations. The study of superaromaticity has mainly been motivated by the general interest of benzenoid versus annulenoid aromaticity. The synthesis of kekulene made it possible to examine the contributions to diatropicity from the global macrocyclic system and the local benzenoid subunits via ^{1}H NMR spectroscopy.[17–19] The inner protons are subjected to opposite fields caused by the induced ring currents of macrocycles and of benzenoid rings. However controversy over whether kekulene is superaromatic still exists.[2,3] Cioslowski *et al.*[1] calculated superaromatic stabilization energy for the kekulene molecule using a 'superconjugation-free' reference energy determined from a set of benzenoid hydrocarbons. They concluded that kekulene is slightly superaromatic. Later, Aihara asserted that kekulene is non-superaromatic from his graph-theoretical analyses. The suggestion of the annulene-within-an-annulene structure for corannulene tetraanion by Ayalon *et al.*[3] makes this topic even more controversial.

To characterize superaromaticity, reference structures have to be chosen in such a way that they can account for contributions from all components except those involving the global conjugation. Cioslowski *et al.*'s way of accomplishing this is to use a so-called additive nodal increments model. In this model the 'superconjugation-free' energy is decomposed into contributions of localized benzene rings (the nodes).[1] The calculation was at the Hartree–Fock level, although the model itself was derived from studies at the Hückel level.[20,21] This definition of reference structure for superaromaticity is comparable to Dewar's definition of reference structure for aromaticity.[5] If the same procedure is applied to kekulene using energies from Hückel calculations, a problem arises, that is, the fitting error to obtain the 'superconjugation-free' energy is comparable to the superaromatic stabilization energy itself (the energy difference between kekulene molecule and its 'superconjugation-free' reference structure). The superaromaticity or superantiaromaticity so obtained may result from this numerical fitting error. The same problem of fitting error exists when one tries to subtract the 'superconjugation-free' resonance energy from the total kekulene resonance energy. Three parameters as defined in Ref. 2 are fitted, by least-squares fitting, to the set of all fragment benzenoid molecules of kekulene or to a subset of this set. This is done for both E(Hückel) and TRE. Note that the definition of superaromaticity based on the total energy is different from the one based on the resonance energy. Of course, introducing more parameters, as Hess and Schaad[6] did to the aromaticity case may reduce this fitting error. Nevertheless, the relative smallness of superaromaticity as compared with the benzenoid aromaticity still poses a problem. This can be seen from the calculations and discussions in Aihara's paper.[2] Hence a good superaromaticity index should be sensitive enough to detect this small part of the aromaticity.

We first re-examine the annulenoid aromaticity using different indices with different reference structures, in order to test the sensitivities of the aromaticity indices. The reference structures chosen for this purpose are polyene and topologically defined acyclic structure.[7,8] The aromaticity indices tested are resonance energy (RE) and relative hardness η_r,[12] in four combinations: (i) RE with polyene reference structure; (ii) RE with acyclic reference structure (TRE); (iii) relative hardness with polyene reference structure and (iv) relative hardness with acyclic reference structure. All these quantities can be calculated analytically. The essential conclusions are as follows. RE can be used as an aromaticity index only if correct reference structures are used. Whereas RE with polyene reference structure leads to correct predictions only for $(4n+2)$ annulenes, TRE gives predictions consistent with the $(4n+2)$ rule, $(4n+2)$ annulenes being aromatic and $4n$ annulenes being antiaromatic. The relative hardness index with either reference structure gives correct predictions for all annulenes. Therefore, relative hardness as an aromaticity index is less sensitive to the reference structure used. That is, deviations caused by incorrect reference structures play a lesser role when the relative hardness is used. This conclusion turns out to be crucial in measuring superaromaticity because of its relative smallness compared with total aromaticity. This relative independence of reference structure makes the relative hardness a more sensitive index for superaromaticity.

We now proceed to the problem of determining the superaromaticity of kekulene, coronene and corannulene tetraanion using a relative hardness index. The reference molecule for kekulene is a benzenoid compound with the same number of benzene rings, two more carbon atoms and no macrocycles. The geometry of the reference molecule is chosen in such a way that it overlaps with the kekulene molecule completely except for the two terminal benzene rings, which overlap with each other partially. The reference molecules for coronene and corannulene tetraanion are similarly defined. A *super-relative hardness* index is defined as

$$\eta^{s}_{r1} = \eta_{r}(\text{molecule}) - \eta_{r}(\text{reference structure}) \qquad (1)$$

If a molecule has a greater relative hardness than its reference molecule then the molecule is more aromatic than its reference molecule. The extra aromaticity is the superaromaticity. Hences a positive η^{s}_{r1} means superaromaticity and a negative η^{s}_{r1} signifies superantiaromaticity. Values of η^{s}_{r1} for kekulene, coronene and corannulene tetraanion are $0{\cdot}0836|\beta|$, $0{\cdot}0097|\beta|$ and $0{\cdot}2196|\beta|$, respectively. Kekulene, coronene and corannulene tetraanion are predicted to be superaromatic. Note that the η^{s}_{r1} value for corannulene tetraanion is fairly large, which signifies the importance of annulenoid conjugation in this molecule. The corresponding differences of TREs per π-electron are $-0{\cdot}0009|\beta|$, $0{\cdot}0018|\beta|$ and $0{\cdot}0457|\beta|$ respectively. These numbers from TRE values cannot be used to predict superaromaticity because the reference structures used here have some flaws. That is, they cannot represent faithfully the 'superconjugation-free' part of the molecule. Nevertheless, η^{s}_{r1} is expected still to be useful because of its relative independence of reference structure.

To do a more satisfactory job, to represent faithfully the 'superconjugation-free' part of a superaromatic molecule, a superaromatic reference structure can be defined topologically for the molecule. This reference structure is given, as in the general aromaticity case,[7,8] by a secular polynomial derived from the secular polynomial of the superaromatic molecule. The difference between the two secular polynomials is that the reference polynomial, denoted as $P^{s}_{ac}(x)$, does not contain the terms with contributions from macrocycles whereas the molecular polynomial does. It is straightforward, although tedious, to derive the reference polynomial. The reference polynomials for the three molecules are given in the Appendix. The roots of the polynomial can be found via a combination of net search and bisection methods. Unfortunately, the roots are not all real (see also Ref. 22). Nevertheless, important information can be drawn from these roots. First, only a few roots have non-zero imaginary parts and these parts are all near zero. This allows considerations of either only the real parts or the absolute values of the roots. The energy levels can be ordered. Second, the eigenvalues corresponding to the HOMO and the LUMO obtained are real for both reference polynomials. Hence the hardnesses are still valid quantities to be used in describing superaromaticity, although the total energies and the resonance energies are not so useful in this case. The hardnesses for the superaromatic reference structures of kekulene, coronene and corannulene tetraanion, η^{s}_{ac} are $0{\cdot}4106|\beta|$, $0{\cdot}4648|\beta|$ and $0{\cdot}1583|\beta|$, respectively. Another super-relative hardness then can be defined as

$$\eta^{s}_{r2} = \eta - \eta^{s}_{ac} \qquad (2)$$

Again, a positive η^{s}_{r2} signifies superaromaticity and a negative η^{s}_{r2} indicates superantiaromaticity. Values of η^{s}_{r2} for kekulene, coronene and corannulene tetraanion are $0{\cdot}0266|\beta|$, $0{\cdot}0744|\beta|$ and $0{\cdot}1031|\beta|$ respectively. Hence the η^{s}_{r2} index predicts that all three molecules are superaromatic and the superaromaticity increases from kekulene to coronene to corannulene tetraanion. This prediction agrees with the general chemical intuition. One of the macrocycles in corannulene is a cyclopentadienyl anion.[3] One of the macrocycles in coronene happens to be a benzene ring. Also both species are known to contribute significantly to aromaticity. The larger annulenoid rings of macrocycles in kekulene are expected to contribute much less to aromaticity.

Compared with the corresponding relative hardness, which measures the total aromaticity, super-relative hardnesses for kekulene and coronene are seen to be small, but nevertheless sensible, numbers. However, the value for corannulene tetraanion is large. Again, this indicates decisively that annulenoid conjugations contribute significantly to aromaticity. Note that the confusion caused by the numerical errors like the fitting errors disappeared here. The disadvantage is that the physical meaning of the reference structures is not that clear, an old problem associated with all topological definitions of reference structures.[23-25]

Another way to assess superaromaticity is to introduce the hypothetical superantiaromatic counterpart of a superaromatic molecule. The superantiaromatic molecule is built as follows:[2] start with the chemical graph[26] of the superaromatic molecule; change bond parameters from 1 to -1 (from bonding to antibonding) for two chemical bonds which are chosen in such a way that they belong to the same benzene ring, and one of them is in the inner macrocycle and the other in the outer macrocycle. Now, any cyclic path in this new graph changes sign twice or not at all if the path is not one of the macrocycles, and macrocycles change sign once. Therefore, the effects of this sign change are only related to those components with macrocyclic contributions. Other terms are unaffected. Define

$$\eta^{s}_{r3} = \eta(\text{superaromatic}) - \eta(\text{superantiaromatic}) \qquad (3)$$

and

$$\Delta E_{\text{Möbius}} = -\tfrac{1}{2}\,[E(\text{seperaromatic}) - E(\text{superantiaromatic})] \qquad (4)$$

The subscript Möbius is used since any global cycle in superantiaromatic molecule is a Möbius ring. The calculated results for the three molecules are as follows:

	$\Delta E_{\text{Möbius}}$	η^{s}_{r3}
kekulene	$0{\cdot}0035\lvert\beta\rvert$	$0{\cdot}0230\lvert\beta\rvert$
coronene	$0{\cdot}0968\lvert\beta\rvert$	$0{\cdot}0216\lvert\beta\rvert$
corannulene tetraanion	$0{\cdot}5208\lvert\beta\rvert$	$0{\cdot}2415\lvert\beta\rvert$

Hence both $\Delta E_{\text{Möbius}}$ and η^{s}_{r3} predict the three molecules to be superaromatic. Superconjugations in corannulene tetrnnnion are significant, as evidenced by large values of both $\Delta E_{\text{Möbius}}$ and η^{s}_{r3}. Note that the two energy components in the energy index used here have, in principle, the same non-superconjugation component and opposite superconjugation component. $\Delta E_{\text{Möbius}}$ is not the superconjugative part of the TRE and hence should not be compared with the TRE. It is easy to see that $\Delta E_{\text{Möbius}}$ is not the same as the TRE from the results for annulenes, which again can be derived analytically.

It is interesting that for the neutral corannulene molecule both $\Delta E_{\text{Möbius}}$ and η^{s}_{r3} are zero, which implies that there are no contributions to aromaticity from the global conjugation. This is in agreement with our chemical intuition. To make both inner and outer rings a $(4n+2)$e ring, charge separation is needed. For example, to obtain a 5C/6e inner ring and 15C/14e outer ring one electron has to be moved from the outer ring to the inner ring. The strong electrostatic interactions resulting from this charge separation will favor the reverse of the process. Hence, in neutral corannulene local benzenoid conjugation dominates.

In conclusion, hardness indices are more sensitive than resonance energy indices and are suitable for the prediction of superaromaticity. All three molecules are predicted to be superaromatic from the three super-relative hardness indices [see equations (1), (2) and (3)] introduced here. The unambiguous prediction of the corannulene tetraanion to be superaromatic provides further theoretical support to the suggestion that there exists an 'annulene-within-an-annulene' structure for this tetraanion. The four negative charges make the molecule more like a 5C/6e ring within a 15C/18e ring. The contributions of the macrocyclic conjugations to aromaticity of the molecule are significant.

ACKNOWLEDGEMENTS

Support from the National Science Foundation to the University of North Carolina at Chapel Hill is gratefully acknowledged. The advice and help of Professors Robert G. Parr and Lawrence T. Scott are appreciated.

REFERENCES

1. J. Cioslowski, P. B. O'Connor and E. D. Fleischmann, *J. Am. Chem. Soc.* **113**, 1086–1089 (1991).
2. J.-I. Aihara, *J. A, Chem. Soc.* **114**, 865–868 (1992).
3. A. Ayalon, M. Rabinovitz, P.-C. Cheng and L. T. Scott, *Agnew. Chem., Int. Ed. Engl.* **31**, 1636–1637 (1992).
4. Z. Zhou, *Int. Rev. Phys. Chem.* **91**, 789–795 (1969).
5. M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.* **913**, 789–795 (1971).
6. B. A. Hess, Jr, and L. J. Schaad, *J. Am. Chem. Soc.* **93**, 305–310 (1971).
7. J.-I. Aihara, *J. Am. Chem. Soc.* **98**, 2750–2758 (1976).
8. I. Gutman, M. Milyn and N. Trinajstić, *J. Am. Chem. Soc.* **99**, 1692–1704 (1977).
9. M. Randić, *Chem. Phys. Lett.***38**, 68 (1976); *J. Am. Chem. Soc.* **99**, 444–450 (1977).
10. W. C. Herndon, *J. Am. Chem. Soc.* **95**, 2404–2406 (1973).
11. Z. Zhou, R. G. Parr and J. F. Garst, *Tetrahedron Lett.* 4843–4846 (1988).
12. Z. Zhou and R. G. Parr, *J. Am. Chem. Soc.* **111**, 7371–7379.
13. S. S. Shaik, P. C. Hiberty, J.-M. Kefour and G. Ohanessian. *J. Am. Chem. Soc.* **109**, 363–374 (1987) and references cited therein for ofiginal doubt.
14. E. D. Glendening, R. Faust, A. Strietwieser, K. P. C. Vollhardt and F. Weinhold, *J. Am. Chem. Soc.* **115**, 10952–10957 (1993) and references cited therein for counter-doubt.
15. R. McWeeny, *Proc. Phys. Soc., London, Sect. A*, **64**, 261, 821 (1951).
16. L. Pauling, *J. Chem. Phys.* **4**, 673–677 (1936).
17. H. A. Staab and F. Diederich, *Chem. Ber.* **116**, 3487–3503.
18. H. A. Staab, F. Diederich, C. Krieger and D. Schweitzer, *Chem. Ber.* **116**, 3504–3512 (1983).
19. H. Vogler, *J. Mol. Struct.* **122**, 333–341 (1985).
20. J. Cioslowski, *Theor. Chim. Acta* **68**, 315.
21. J. Cioslowski, **Chem. Phys. Lett.3 122**, 234 (1985).
22. W. C. Herndon, *J. Am. Chem. Soc.* **104**, 3541–3542 (1982).
23. I. Gutman, *Chem. Phys. Lett.* **66**, 595–597 (1979)
24. I. Gutman and B. Mohar, *Chem. Phys. Lett.* **69**, 375–377 (1980); **77**, 567 (1981).
25. E. Heilbronner, *Chem. Phys. Lett.* **85**, 377–380 (1982).
26. A. Tang, Y. S. Jiang, S. G. Yan and S. S. Dai, *Graph Theory of Molecular Orbitals.* Academic Press, Beijing (1980). N. Trinajstić, *Chemical Graph Theory*, CRC Press, Boca Raton, FL (1983).

APPENDIX

The superaromatic reference polynomial for zekulene is

$$\begin{aligned} P^{s}_{ac}(x) = {} & x^{48} - 60x^{46} + 1672x^{44} - 28794x^{42} \\ & + 343843x^{40} - 3027630x^{38} + 20405407x^{36} \\ & - 107852224x^{34} + 454378157x^{32} \\ & - 1542506250x^{30} + 4248686872x^{28} \\ & - 9530956064x^{26} + 17431940917x^{24} \\ & - 25959111788x^{22} + 31356579259x^{20} \end{aligned}$$

$$\begin{aligned}&- 30530082182x^{18} + 23743496383x^{16}\\ &- 14568993572x^{14} + 6939154846x^{12}\\ &- 2510929054x^{10} + 670534833x^{8}\\ &- 126827418x^{6} + 15938692x^{4}\\ &- 1185048x^{2} + 39204 \qquad \text{(A1)}\end{aligned}$$

The superaromatic reference polynomial for coronene is

$$\begin{aligned}P^{s}_{ac} = {}& x^{24} - 30x^{22} + 387x^{20} - 2828x^{18} + 12991x^{16}\\ &- 39364x^{14} + 80293x^{12} - 110454x^{10}\\ &+ 101034x^{8} - 59508x^{6} + 21274x^{4}\\ &- 4112x^{2} + 320 \qquad \text{(A2)}\end{aligned}$$

The superaromatic reference polynomial for corannulene tetraanion is

$$\begin{aligned}P^{s}_{ac} = {}& x^{20} - 25x^{18} + 260x^{16} - 1475x^{14} + 5030x^{12}\\ &- 10704x^{10} + 14265x^{8} - 11610x^{6} + 5435x^{4}\\ &- 1300x^{2} + 121 \qquad \text{(A3)}\end{aligned}$$