0.25–0.37) afforded a material which was found to consist of approximately 65% of **5**, 25% of **3**, and a remaining unidentified product by NMR spectroscopy. The starting material could be selectively removed by crystallization from 2-propanol. The filtrate, after concentration and two crystallizations (ethyl acetate/hexane) gave **5**: 61 mg (7%); mp 155–157 °C; IR (KBr) 2915, 1582, 1445, 1405, 1325, 1195, 1090, 995, 880, 865, 805 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 2.5–3.23 (m, 8 H), 4.55 (s, 1 H), 6.65 (m, 2 H), 7.0 (m, 2 H); MS, *m/e* 199 ($M^+$), 104, 92, 79. Anal. Calcd for $C_{13}H_{13}NO$: C, 78.39; H, 6.53; N, 7.03. Found: C, 78.60; H, 6.71; N, 7.01.

**2,11-Dithia[3.3](3,5)isoxazolometacyclophane (6).** A solution of **2** (2.25 g, 13.55 mmol) and *m*-xylenedithiol (2.25 g, 13.23 mmol) in benzene (200 mL) was added, over a period of 14 h and under $N_2$, to a refluxing solution of ethanol (1 L) containing KOH (1.5 g). After being stirred for an additional 4 h, the reaction mixture was filtered through Celite, and the filtrate was concentrated to give a crude solid. This was chromatographed (silica gel, $CHCl_3$) and furnished **6**: 1.736 g (48.7%); mp 147–149 °C ($C_2H_5OH/CH_2Cl_2$); IR (KBr) 3115, 2930, 1605, 1426, 1400, 1280, 1218, 1135, 1003, 932, 843, 795 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 3.53–3.9 (m, 8 H), 6.08 (s, 1 H), 6.56 (br s, 1 H), 6.86–7.30 (m, 3 H); MS, *m/e* 263 ($M^+$), 109, 91. Anal. Calcd for $C_{13}H_{13}NOS_2$: C, 59.31; H, 4.94; N, 5.32; S, 24.33. Found: C, 59.47; H, 4.99; N, 5.28; S, 24.63.

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**Registry No.** **1**, 40630-12-4; **2**, 84987-94-0; **3**, 84987-95-1; **4**, 84987-96-2; **5**, 84987-97-3; **6**, 84987-98-4; **7**, 84987-99-5; *p*-xylenedithiol, 105-09-9; *m*-xylenedithiol, 41563-69-3; $NH_2OH\cdot H_2SO_4$, 10046-00-1; $(MeO)_3P$, 121-45-9.

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# A Bond Order Approach to Ring Current and Aromaticity

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An alternative approach to ring current and aromaticity is developed related to bond order. The concept is general enough to include nonplanar and nonbenzenoid rings as well as ions. Calculations are performed with the semiempirical MO method SINDO1 on a representative large number of mono- and polycyclic ring systems up to four rings. Also some excited states are investigated. Most conclusions about aromaticity are in agreement with those reached by a topological index based on resonance energies. Exceptions to this agreement are also presented and explained.

The concept of aromaticity can be found in any textbook of theoretical organic chemistry.[1,2] A conjugated ring system is usually called aromatic if its stability is considerably increased compared to that of its classical localized structure. In the elementary discussion, much attention is given to the Hückel rule that a ring system with $4n + 2$ electrons is aromatic, whereas a system with $4n$ electrons is not. Aromatic systems in this sense are benzene, pyridine, pyrrole, furan, cyclopentadienyl anion, etc. However, more sophisticated arguments have to be given when it comes to the point of comparing the degree of aromaticity. Difficulties with the Hückel rule arise with the aromaticity of larger annulenes. Dewar[2] emphasizes that resonance energies calculated by the Hückel method cannot be used as indices for classification of aromaticity. He advances the idea of resonance energies in an SCF framework referring to standard bond energies of ficticious single and double bonds in rings. His result is that from the $n$-annulenes, the compounds with $n = 6$ and 10 are aromatic, those with $n = 4$ and 8 are antiaromatic, and the rest are slightly aromatic or nonaromatic. The situation was comprehensively reviewed by Bergmann and Agranat[3] in 1970. From the ten criteria for aromaticity summarized in their article we shall concentrate only on the following important ones: (1) Lack of reactivity with respect to addition reactions, (2) very low enthalpy of the ground state, (3) sustained induced ring current.

In particular, we shall show that lack of bond alternation is not a necessary nor sufficient criterion for aromaticity. More recently a graph-theoretical approach to aromaticity has been advanced. Trinajstić and co-workers[4] have defined a topological resonance energy and applied this method successfully to hydrocarbons. Aihara[5] extended the graph-theoretical approach to unusual ions. His recent work[6] is addressed to the question of whether oxocarbon dianions are really aromatic. In the following section we develop an alternative approach to aromaticity based on the ring current concept. We relate ring current and bond order. We present an application of this concept to more than 70 ring systems. These include monocyclic and polycyclic rings, exotic systems, and excited states. We suggest that the graph-theoretical approach by Aihara can be misleading in crucial cases.

## Method

Several years ago, we introduced a maximum bond order principle[7] which results in the definition of a bond order between any pair of atoms in a molecule, once an LCAO MO wave function is obtained by an ab initio or semiempirical MO method. We showed that the principle can be applied to CI wave functions[8] for which a density matrix in the LCAO framework can be defined. The bond order is the weighted sum of eigenvalues of the two-center parts of the density matrix of the pair of atoms considered.

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(1) Streitwieser, A. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961.

(2) Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969.

(3) Bergmann, E. D.; Agranat, I. "Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity"; The Jerusalem Symposia on Quantum Chemistry and Biochemistry III; Bergmann, E. D.; Pullman, B., Eds.; Israel Academy of Sciences and Humanities: Jerusalem, 1971; p 9 ff.

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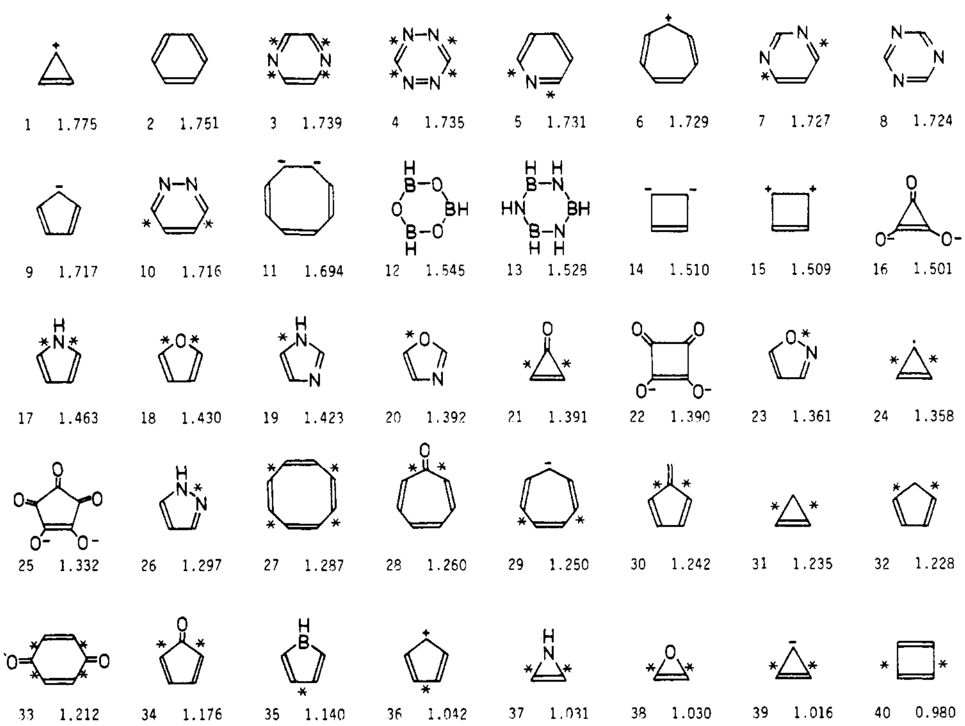

**Figure 1.** Ring current index of monocyclic ring systems; the weakest bonds are marked with asterisk.

Because of discontinuities in the resulting bond order, we later abandoned the Mulliken overlap definition of bonding and defined the weighting factor by a projection technique in Hilbert space.[9] We now suggest this bond order can provide a useful tool in classifying aromatic compounds. From a consideration of six-membered rings like benzene, pyridine, borazine, and similar systems it appears that an aromatic compound tries to reduce the alternation in bond length between single and double bonds of a classical structure as much as possible. However, introduction of heteroatoms usually poses a limit to this tendency as can be seen from pyrrole, furan, or oxazole. Furthermore, the standard bond lengths of single and double bonds are different for different atoms. Thus we cannot easily tell from the final geometry of a compound how much bond alternation has been reduced. The concept of bond order does not suffer from this deficiency. Here, we can in a single reference frame go gradually from a single bond to a double bond; e.g., an NN double bond and a CC double bond both have a bond order value close to 2. We now want to consider the idea of a ring current in this context. It seems obvious that the magnitude of a ring current is determined by its weakest link in the ring. We consider the weakest link as the bond with the lowest bond order. So we now define the minimal bond order in a ring system in its equilibrium as an index of aromaticity based on ring current. In the case of polycyclic ring systems, we distinguish rings sharing a bond and rings linked by a bond. In these cases we neglect those bonds which induce opposite ring currents in adjacent rings or linkages which cannot exhibit ring current. The bond orders are not $\pi$-electron bond orders; hence, the concept is not limited to planar systems. This means that effects of changes in geometry due to substituents can be traced without relying on topology only. As we shall see in the section on application, this is a definite advantage over parameterized methods. In this sense, we would also like to emphasize that this concept is simple enough to include nonplanar and nonbenzenoid compounds as well as radicals and ions. In some cases the topological resonance energy method faces difficulties because the structure of the compound and the energy of a fictitious acyclic polyene-like reference structure have to be known. The above-mentioned concept is also definitely different from structure–reactivity relationships of addition reactions. In such cases the maximum bond order is the reactive one. We shall show in the following that this criterion for aromaticity has definite disadvantages.

## Monocyclic Rings

Since our interest in this matter came from a consideration of aromatic compounds which were recently discussed, namely, the oxocarbon dianions,[6] we included a large variety of well-known rings in this study for comparison and ordered them in the sequence of our ring current index. Calculations were performed with the semiempirical MO method SINDO1. Bond orders were determined for the optimized structures in their ground-state equilibrium according to the maximum bond order principle[7] with projected weighting factors.[9] The results for this index are in Figure 1. The complete set of bond orders is in Table I. Keeping in mind that the standard single bond order in ethane is 1.254 and that the standard double bond order in ethylene is 2.155, we may separate the compounds into the following five groups: (a) aromatic compounds, cyclopropenyl cation (1.775) to $C_8H_8^{2-}$ (1.694); (b) moderately aromatic compounds, $H_3B_3O_3$ (1.548) to $C_5O_5^{2-}$ (1.332); (c) nonaromatic compounds, pyrazole (1.297) to quinone (1.212); (d) moderately antiaromatic compounds, cyclopentadienone (1.176) to $H_4C_4BH$ (1.140); (e) antiaromatic compounds, cyclopentadienyl cation (1.042) to cyclobutadiene (0.98). Detailed observations are the following: (1) Cyclopropenyl cation (1.775) has an even higher degree of aromaticity than benzene (1.751). (2) Six-membered rings isoelectronic with benzene are considerably more aromatic than five-membered rings. They range from 1.739 in pyrazine to 1.528 in borazine compared to 1.717 in cyclopentadienyl anion to 1.297 in pyrazole. (3)

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(10) Nanda, D. N.; Jug, K. *Theor. Chim. Acta* **1980**, *57*, 95.
(11) Jug, K.; Nanda, D. N. *Theor. Chim. Acta* **1980**, *57*, 107, 131.

Table I. Bond Orders of Ring Bonds[a]

| compd | bond order | | | | |
|---|---|---|---|---|---|
| | 1-2 | 2-3 | 3-4 | 4-5 | 5-1 |
| 1 | 1.775 | 1.775 | | | |
| 2 | 1.751 | 1.751 | 1.751 | 1.751 | |
| 3 | 1.744 | 1.739 | 1.739 | 1.744 | |
| 4 | 1.790 | 1.735 | 1.735 | 1.790 | |
| 5 | 1.731 | 1.745 | 1.752 | 1.752 | |
| 6 | 1.729 | 1.729 | 1.729 | 1.729 | |
| 7 | 1.748 | 1.727 | 1.728 | 1.728 | |
| 8 | 1.724 | 1.724 | 1.724 | 1.724 | |
| 9 | 1.717 | 1.717 | 1.717 | 1.717 | 1.717 |
| 10 | 1.791 | 1.716 | 1.757 | 1.739 | |
| 11 | 1.694 | 1.694 | 1.694 | 1.694 | |
| 12 | 1.545 | 1.545 | 1.545 | 1.545 | |
| 13 | 1.528 | 1.528 | 1.528 | 1.528 | |
| 14 | 1.510 | 1.510 | 1.510 | | |
| 15 | 1.509 | 1.509 | 1.509 | | |
| 16 | 1.501 | 1.501 | | | |
| 17 | 1.534 | 1.940 | 1.463 | 1.463 | 1.940 |
| 18 | 1.514 | 1.964 | 1.430 | 1.430 | 1.964 |
| 19 | 1.452 | 1.908 | 1.500 | 1.423 | 1.978 |
| 20 | 1.422 | 1.931 | 1.478 | 1.393 | 1.981 |
| 21 | 1.861 | 1.391 | | | |
| 22 | 1.390 | 1.390 | 1.390 | | |
| 23 | 1.501 | 1.957 | 1.361 | 1.498 | 1.955 |
| 24 | 1.995 | 1.358 | | | |
| 25 | 1.332 | 1.332 | 1.332 | 1.332 | 1.332 |
| 26 | 1.564 | 1.927 | 1.297 | 1.553 | 1.916 |
| 27 | 2.073 | 1.287 | 2.073 | 1.287 | |
| 28 | 2.023 | 1.370 | 2.042 | 1.262 | |
| 29 | 2.071 | 1.250 | 1.932 | 1.557 | |
| 30 | 1.293 | 2.068 | 1.242 | 1.242 | 2.068 |
| 31 | 2.166 | 1.235 | | | |
| 32 | 1.309 | 2.056 | 1.228 | 1.228 | 2.056 |
| 33 | 2.080 | 1.212 | 1.212 | 2.080 | |
| 34 | 1.252 | 2.095 | 1.170 | 1.170 | 2.095 |
| 35 | 1.140 | 2.058 | 1.280 | 1.280 | 2.058 |
| 36 | 1.042 | 2.014 | 1.435 | 1.435 | 2.014 |
| 37 | 2.044 | 1.031 | | | |
| 38 | 2.274 | 1.030 | | | |
| 39 | 2.029 | 1.016 | | | |
| 40 | 2.039 | 0.980 | 2.039 | | |

[a] The atoms of Figure 1 are numbered counterclockwise from the lower left corner.

*The ring current decreases the closer two nitrogen atoms or one nitrogen and one oxygen atom are in the ring.* Pyridazine (1.716) is less aromatic than pyrazine (1.739) or pyrimidine (1.727), pyrazole (1.297) is less aromatic than imidazole (1.423), and isoxazole (1.361) is less aromatic than oxazole (1.392). This observation can be explained by the weakening of a bond containing a heteroatom with a lone pair. (4) The oxocarbon dianions are only moderately aromatic with a bond order of 1.50 for the three-membered ring as the highest value, which is on the order of borazine (1.528). All oxocarbon dianions have equal ring bond lengths as can be seen from Table I. The aromaticity decreases rapidly with increasing ring size, so that no aromaticity is expected for rings with six or more atoms. This conclusion is basically in agreement with Aihara,[6] who set the limit at the three-membered ring. (5) Cyclooctatetraene (1.287) appears in a tublike nonplanar geometry as nonaromatic similar as tropone (1.260), whereas resonance-energy calculations define cyclooctatetraene as antiaromatic.[2,4] We explain this by the reduction in the single bond length which is substantially shorter (exptl[12] 1.47 Å, calcd 1.50 Å) than a standard single bond. The situation here appears to be quite different from the one in planar cyclobutadiene where the bond alternation is greatly pronounced, which makes the latter compound the most antiaromatic in this series. (6) In odd-membered annulenes the aromatic ions have antiaromatic counterparts when two electrons are added or removed. Whereas the aromaticity is maintained up to seven-membered rings, antiaromaticity drops quickly to nonaromaticity with increasing ring size. When we compare the results for single molecules with data in the literature, in most cases there is agreement [e.g., pyrrole (1.463) being more aromatic than furan (1.430) was also found by Cordell and Boggs[13]] or quantitative disagreement as in the cases of cyclooctatetraene and cycloheptatrienyl anion which are sometimes considered to be slightly antiaromatic, whereas we find them nonaromatic. Also, we find cyclopropenone to be moderately aromatic whereas Aihara[6] and others classify it as aromatic. However, the following qualitative disagreement is more serious. From his Hückel calculation of the resonance energies of oxocarbon rings, Aihara[6] concluded that the neutral three-membered oxocarbon ring is aromatic or nonaromatic. We performed a calculation on this system which resulted in a fragmentation of $C_3O_3$ into three much more stable CO molecules. A bond order analysis at a typical CC distance of 1.50 Å reveals that the CC bond order in the rings is about 0.85. This would classify the $C_3O_3$ as antiaromatic if it existed. We believe that the removal of two electrons changes the system *drastically and that an unfortunate parametrization in the topological method is the cause for the wrong conclusion.* We want to emphasize here that modifications in geometry have often no major impact on bond orders, hence ring currents. The planar cyclooctatetraene stays nonaromatic, and the cyclopentadienyl cation stays antiaromatic even in $D_{5h}$ symmetry. In the latter case the bond orders are still indicating alternation of bonds. This means that geometry is not the governing factor in bonding but that bond orders are much more indicative for aromaticity. This difference does not show up in standard hydrocarbons. For instance, we also present ring current indices for methylenecyclopropene (**41**, 1.386), 3-radialene (**42**, 1.218), dimethylenecyclobutene (**43**, 1.098), and 4-radialene (**44**, 1.187) and find them similar to the results of the topological resonance energy method. In the nine-membered rings $C_9H_9^-$ (**45**, 1.66), $C_8H_9N$ (**46**, 1.425), and $C_8H_8O$ (**47**, 1.402) we find similar trends as in the five-membered rings. We cannot substantiate a significant ring current difference between azonine and oxonine. The ten-membered ring $C_{10}H_{10}$ (**48**) shows bond alternation, but its ring current index (1.463) classifies it as moderately aromatic. We finally have to criticize the criterion for aromaticity based on addition reactions: (1) There is no straightforward distinction between nonaromatic and antiaromatic compounds. Fulvene with maximum bond order 2.068 appears as more reactive than cyclobutadiene with a maximum bond order 2.039. (2) If the maximum bond order is below that of benzene (1.751), e.g., in $B_3N_3H_6$ (1.528) or $C_5O_5^{2-}$ (1.332), the compound should be less reactive toward addition of olefins and hence more aromatic. Both results seem unacceptable. We present a comprehensive comparison of ring current (RC) and topological resonance energy (TRE, RE) indices in Table II. Except for $C_3H_3$, which we find to be close to nonaromatic compared to being antiaromatic in TRE, the agreement is satisfactory. Unfortunately, there are no experimental data on ring currents in the literature. It must be realized that the often quoted NMR chemical shifts do not correlate well with ring current aromaticity; furan has a higher

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[12] Fray, G. I.; Saxton, R. G. "The Chemistry of Cyclo-octatetraene and Its Derivatives"; Cambridge University Press: Cambridge, 1978; p 9.

[13] Cordell, F. R.; Boggs, J. E. *THEOCHEM* **1981**, *2*, 163.

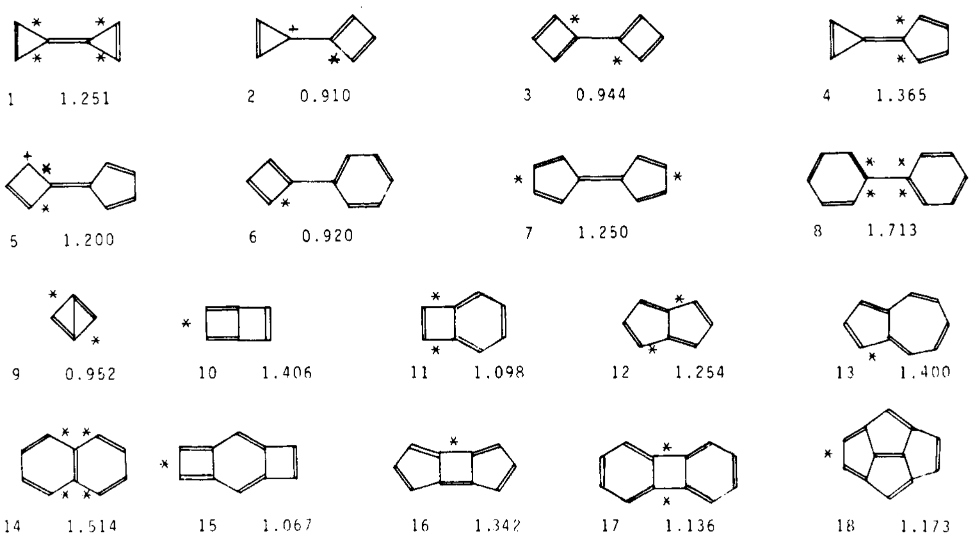

**Figure 2.** Ring current index of polycyclic ring systems; the weakest bonds are marked with asterisk.

Table II. Comparison for Monocyclic Rings

| compd | RC | TRE[a] | RE[b] |
|---|---|---|---|
| 1 | 1.775 | 0.268 | 0.536 |
| 2 | 1.751 | 0.046 | 0.273 |
| 3 | 1.739 | 0.022 | |
| 5 | 1.731 | 0.038 | |
| 6 | 1.729 | 0.032 | |
| 7 | 1.727 | 0.032 | |
| 9 | 1.717 | 0.094 | |
| 11 | 1.694 | | 0.184 |
| 45 | 1.660 | | 0.175 |
| 48 | 1.463 | | 0.159 |
| 17 | 1.463 | 0.040 | |
| 18 | 1.430 | 0.007 | |
| 46 | 1.425 | | 0.134 |
| 19 | 1.423 | 0.033 | |
| 47 | 1.402 | | 0.024 |
| 21 | 1.391 | | 0.164 |
| 41 | 1.386 | 0.016 | |
| 24 | 1.358 | −0.155 | |
| 26 | 1.297 | 0.047 | |
| 27 | 1.287 | | −0.595 |
| 28 | 1.260 | | 0.071 |
| 29 | 1.250 | −0.097 | |
| 30 | 1.242 | 0.003 | 0.020 |
| 42 | 1.218 | 0.002 | 0.009 |
| 44 | 1.187 | −0.009 | −0.072 |
| 34 | 1.176 | | −0.070 |
| 43 | 1.098 | −0.027 | −0.163 |
| 36 | 1.042 | −0.153 | |
| 37 | 1.031 | | −0.725 |
| 38 | 1.030 | | −0.230 |
| 39 | 1.016 | −0.366 | |
| 40 | 0.980 | −0.307 | −1.226 |

[a] Reference 4. [b] References 5 and 6.

chemical shift than pyrrole and naphthalene a higher one than benzene.

## Polycyclic Rings

A selection of 18 hydrocarbons is presented in Figure 2. The first eight compounds contain two rings which are linked by one single or double bond. In each of these rings a ring current can be maintained, but no current can be sustained from one ring to the other. We have therefore neglected this linkage from consideration of the minimum bond order. In asymmetric cases, there is a polarization of the rings which results in a modification of bond orders. If we look for the minimum bond order in both rings to determine aromaticity, we find aromaticity only in compound **8**. Compound **6** would be termed antiaromatic. However, there is substantial ring current in the six-membered ring (1.707), whereas the four-membered ring behaves antiaromatically. We would expect that the overall behavior of the compound is dominated by its antiaromatic component. For the parent rings, it can be said that the six-membered rings exhibit aromaticity, the four-membered rings antiaromaticity, and the three- and five-membered rings nonaromaticity. Charged compounds are modified according to their monocyclic parents. The second set of molecules contains two to four rings adjacent to each other. A ring current can be sustained only along the outer bonds. According to the ring current criterion compounds **10**, **13**, **14**, and **16** are moderately aromatic, **12** is nonaromatic, **11**, **15**, **17**, **18** are moderately antiaromatic, and **9** is antiaromatic. In comparison to the resonance energy work,[4,5] a serious discrepancy arises. These methods classify **10** as highly antiaromatic and **12** as moderately antiaromatic. Our conclusion would be the same if we included the bond common to both rings. These bond orders are 0.742 for **10** and 1.184 for **12**. These bonds are certainly responsible for the destabilization, i.e., loss of resonance energy, but will not show up in the ring current. Another case of interest is compound **17**. We find it to be antiaromatic due to the four-membered ring, whereas its TRE value (Table III) characterizes it as moderately aromatic. This latter result may be due to the fact that the stabilization of two benzene rings outweights the destabilization of the 4-radialene fragment. In all other cases these adjacent neighbor ring bonds are not crucial, and there is qualitative agreement between the topological resonance energy method and the ring current method. We feel that we must now point out an essential difference between our method and the topological resonance energy method. We base our conclusions, e.g., for pentalene on

Table III. Comparison for Polycyclic Rings

| compd | RC | TRE[a] | RE[b] |
|---|---|---|---|
| 8 | 1.713 | 0.042 | 0.502 |
| 14 | 1.514 | 0.039 | 0.389 |
| 10 | 1.406 | (−0.100) | −0.604 |
| 13 | 1.400 | 0.015 | 0.151 |
| 4 | 1.365 | 0.054 | |
| 7 | 1.280 | −0.030 | |
| 12 | 1.254 | −0.027 | −0.215 |
| 1 | 1.251 | −0.077 | |
| 18 | 1.173 | −0.045 | |
| 17 | 1.136 | 0.010 | |
| 11 | 1.098 | −0.049 | |
| 15 | 1.067 | −0.079 | |

[a] Reference 4. [b] References 5 and 6.

the proper symmetry, $C_{2h}$, of this molecule. The MO's of the Hückel method, and hence also the topological method, result in $D_{2h}$ symmetry. So the topological method gives the right answer on the wrong basis.

## Exotic Molecules and Excited States

A system which would pose difficulty to the topological resonance energy method is dehydrobenzene which can formally be presented as consisting of two double bonds and one triple bond. This triple bond cannot be treated in the standard Hückel method which the authors claim as underlying the topological resonance energy.[14] The system is partially delocalized, and its ring current index of 1.535 would classify it as moderately aromatic. If we consider the reactivity for an addition reaction, the maximum bond order of 2.629 would classify it as highly reactive without aromaticity. So, depending on the experiment, the answer will be different for ring current and addition reactions. Even more daring is a treatment of nitrogen rings analogous to benzene and other hydrocarbons. The $N_6$ ring has a uniform bond order of 1.792 and should exhibit substantial ring current. However, it is much less stable than $3N_2$ and will therefore thermodynamically decompose into these fragments. The $N_4$ ring is a rectangle and has ring current index 1.0. It should be antiaromatic and behave similar to cyclobutadiene. We have also investigated $H_2C_2N_2$ (1.006), $H_3C_3N$ (0.938), and $H_2C_2N_2H_2$ (1.025) and find them antiaromatic. From the three-membered rings we find $N_3H^{2+}$ (1.720) aromatic, $N_3H$ (1.240) nonaromatic, and $N_3H^{2-}$ unstable. The nonplanar systems $N_3H_3^{2+}$ (1.01) and $N_3H_3$ (1.14) are antiaromatic, and $N_3H_3^{2-}$ is again unstable. Bond orders can also be helpful to assess the ring current in excited states. We have recently calculated excited-state geometries of pyrrole and furan[15] and of imidazole, pyrazole, pyridine, pyrazine, pyrimidine, pyridazine and *s*-triazine.[16] In pyrrole we find all excited states less aromatic than the ground state. The singlet $S_4$ should even be nonaromatic with respect to ring current. This is also true for most excited states of furan. However, the ring current of $S_2$ of furan should be increased due to the more uniform distribution of bond orders compared to the ground state. In imidazole and pyrazole we find a substantial weakening of bonds in the first three excited states ($T_1$, $S_1$, $S_2$) with minimum bond orders between 1.07 and 1.20, which would classify them as moderately antiaromatic. The six-membered ring containing nitrogen has mostly excited states which are moderately aromatic. But again, aromaticity is in general greatly reduced compared to the ground state.

## Conclusion

We consider aromaticity as a complex phenomenon which cannot be explained by a single index. We have shown that the conclusions reached by ring current investigations can be based on the minimal bond order in a ring system. Only those bonds are considered which can in principle sustain a ring current. Structure–reactivity relationships for addition reactions must be based on the maximum bond order. Their conclusions about the aromaticity of a compound are often quite different from those reached by use of ring currents. Finally, the advantages of the ring current criterion over the stability considerations of topological resonance energies are the following: (1) Aromaticity appears as a localized phenomenon linked to a particular bond compared to the delocalized phenomenon of resonance energy which is a property of the whole molecule. (2) There is no need for a fictitious compound for comparison. (3) The results do not depend on parametrization. (4) The molecular orbitals appear in the right geometry. (5) Unusual systems like $N_6$ or dihydrobenzene can be treated.

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**Registry No.** **1** (monocylic), 26810-74-2; **1** (polycyclic), 1608-08-8; **2** (monocyclic), 71-43-2; **2** (polycyclic), 84988-30-7; **3** (monocyclic), 290-37-9; **3** (polycyclic), 84988-33-0; **4** (monocyclic), 290-96-0; **4** (polycyclic), 6249-23-6; **5** (monocyclic), 110-86-1; **5** (polycyclic), 84988-31-8; **6** (monocyclic), 26811-28-9; **6** (polycyclic), 84988-34-1; **7** (monocyclic), 289-95-2; **7** (polycyclic), 91-12-3; **8** (monocyclic), 290-87-9; **8** (polycyclic), 92-52-4; **9** (monocyclic), 12127-83-2; **9** (polycyclic), 13969-14-7; **10** (monocyclic), 289-80-5; **10** (polycyclic), 1552-98-3; **11** (monocyclic), 34510-09-3; **11** (polycyclic), 4026-23-7; **12** (monocyclic), 289-56-5; **12** (polycyclic), 250-25-9; **13** (monocyclic), 6569-51-3; **13** (polycyclic), 275-51-4; **14** (monocyclic), 36685-24-2; **14** (polycyclic), 91-20-3; **15** (monocyclic), 12240-33-4; **15** (polycyclic), 24447-42-5; **16** (monocyclic), 38926-01-1; **16** (polycyclic), 253-01-0; **17** (monocyclic), 109-97-7; **17** (polycyclic), 259-79-0; **18** (monocyclic), 110-00-9; **18** (polycyclic), 569-40-4; **19**, 288-32-4; **20**, 288-42-6; **21**, 2961-80-0; **22**, 28737-40-8; **23**, 288-14-2; **24**, 60512-06-3; **25**, 15110-70-0; **26**, 288-13-1; **27**, 629-20-9; **28**, 539-80-0; **29**, 34464-18-1; **30**, 497-20-1; **31**, 2781-85-3; **32**, 542-92-7; **33**, 106-51-4; **34**, 13177-38-3; **35**, 287-87-6; **36**, 29661-18-5; **37**, 157-17-5; **38**, 157-18-6; **39**, 20829-57-6; **40**, 1120-53-2; **41**, 4095-06-1; **42**, 3227-90-5; **43**, 5291-90-7; **44**, 3227-91-6; **45**, 45730-23-2; **46**, 293-57-2; **47**, 293-59-4; **48**, 3227-76-7; $N_6$, 7616-35-5; $N_4$, 42851-09-2; $H_2C_2N_2$, 287-32-1; $H_3C_3N$, 287-24-1; $H_2C_2N_2H_2$, 13473-83-1; $N_3H^{2+}$, 84988-32-9; $N_3H$, 157-29-9; $N_3H_3^{2+}$, 73870-52-7; $N_3H_3$, 6572-31-2.

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[14] For criticism of this claim see: Heilbronner, E. *Chem. Phys. Lett.* **1982**, *85*, 377.

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