reduced pressure provided 135 mg of a solid which was sublimed (130 °C, 0.4 mm) to give 46 mg (54% yield) of **18** as a white solid: ^{1}H NMR δ ($CDCl_3$) 2.5–0.8; ^{13}C NMR δ ($CDCl_3$) 71.1 (C-2), 41.7 (C-1), 40.2 (C-3 and C-16), 39.4 (C-12), 38.1 (C-5), 37.2 (C-7 and C-17), 37.2 (C-9), 37.2 (C-8), 32.3 (C-10 and C-18), 31.6 (C-14 and C-15), 31.2 (C-4 and C-6), 29.5 (C-11 and C-13); exact mass calcd for $C_{18}H_{26}O$ 258.198, found 258.197.

Ketone 22. A mixture of alcohol **18** (100 mg, 0.387 mmol), dry lead tetraacetate (343 mg, 0.774 mmol, partially dried by suction filtration under dry nitrogen, then further dried over potassium hydroxide under vacuum, and stored in the dark in a dessicator over phosphorus pentoxide), and iodine (177 mg, 0.700 mmol) in dry benzene (20 mL) was stirred under nitrogen at 80 °C for 20 min and then at 70–75 °C for an additional 2 h. The reaction mixture was then allowed to cool to room temperature, and the inorganic salts that precipitated were filtered and washed with ether. The filtrate and the ether washings were combined and shaken with a saturated aqueous solution of sodium thiosulfate (30 mL) until the solution was decolorized. The layers were then separated, and the organic layer was washed with water (2 × 10 mL) and saturated aqueous sodium bicarbonate (2 × 10 mL) and then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure with no external heating provided the crude oily iodo ketone **20** which was used immediately in the next step.

A solution of lithium bis(trimethylsilyl)amide was prepared by the dropwise addition of *n*-butyllithium (2.0 mmol) to a stirred solution of 1,1,1,3,3,3-hexamethyldisilazane (0.42 mL, 2.0 mmol) in anhydrous tetrahydrofuran (15 mL), which was maintained at 0 °C under nitrogen. The reaction mixture was stirred at 0 °C for 1 h and then it was cooled to −78 °C. A solution of the crude iodo ketone **20** and hexamethylphosphoramide (0.75 mL) in anhydrous tetrahydrofuran (5 mL) was then added dropwise. The resulting solution was stirred for 1 h at −78 °C, for 3 h at −30 °C, and for 2 h at 0 °C. At this point the reaction mixture was quenched with water (2 mL) and diluted with ether (30 mL). The layers were separated, and the organic layer was washed with brine (4 × 20 mL) and then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave 96 mg of a tan solid which was sublimed (105 °C (0.5 mm)) to provide 84 mg (84% yield) of **22** as a white solid: ^{1}H NMR δ ($CDCl_3$) 2.81–2.68 (m, 1 H, CHC=O), 2.57–1.08 (br m, 23 H); ^{13}C NMR δ ($CDCl_3$) 218.0 (s), 50.2 (d), 47.3 (s), 42.8 (t), 40.5 (t), 40.3 (d), 39.3 (s), 39.1 (t), 38.7 (t), 37.4 (t), 37.2 (t), 37.0 (d), 36.5 (t), 33.3 (d), 32.1 (t), 31.9 (t), 28.8 (d), 27.7 (d); IR ν (CCl_4) 2920, 2870, 1699, 1470, 1330, 1255 cm^{-1}; exact mass calcd for $C_{18}H_{24}O$ 256.183, found 256.181.

Acknowledgment. This work was supported by grants from the United Parkinson Foundation and the University of Delaware Research Foundation.

Registry No. 2, 49624-70-6; **6**, 92013-38-2; **7**, 92013-39-3; **8**, 92013-40-6; **9**, 92013-41-7; **10**, 92013-42-8; **15/16**, 92013-43-9; **18**, 92013-44-0; **19**, 92013-45-1; **20**, 92013-46-2; **21**, 92013-47-3; **22**, 92013-48-4; **23**, 92013-49-5; lead tetraacetate, 546-67-8.

Aromaticity in Unusual Heteropolar Monocyclic Rings with $(4n + 2)$ π Electrons

Karl Jug

Theoretische Chemie, Universität Hannover, Callinstr. 3A, 3000 Hannover 1, Federal Republic of Germany

Received April 23, 1984

SINDO1 calculations are performed on selected heteropolar monocyclic ring systems with three to eight atoms containing $(4n + 2)$ π electrons in the ring in the ground-state equilibrium. Different from Hückel's $(4n + 2)$ rule which declares these systems as aromatic, an alternative ring current criterion predicts a whole scale of aromaticity indexes ranging from aromatic to antiaromatic. The smallest planar aromatic ring $Be(CH)_2$ and the smallest nonplanar aromatic ring $(BeCH)_2$ are presented.

1. Introduction

It is widely believed that a ring system of $4n + 2$ π electrons is aromatic. This famous Hückel rule is the basis for every discussion of aromatic systems.[1,2] Most of the arguments and proofs or disproofs are related to calculations with Hückel's π-electron method. Since the results of the more refined versions[3-5] are essentially topological, they work best for hydrocarbons. It is not surprising that the early discussion, which was very nicely presented in 1961 by Streitwieser,[6] focuses on hydrocarbons and substituted systems. Exceptions from Hückel's rule were discovered in polycyclic rings. In monocyclic rings the effect of a substituent outside of the ring had to be considered. Whereas fulvene was considered initially as aromatic[6] and later as nonaromatic, the cyclopentadienone was considered as antiaromatic due to its CO bond polarization toward oxygen. The simplest explanation was that four π electrons were left in the ring. For the same reason cyclopropenone should be more aromatic than methylenecyclopropene. The question of aromaticity in these compounds was recently raised again by Greenberg et al.,[7] who gave evidence of a moderate aromaticity in cyclopropenone through reexamination of strain energy. Nothing definitive can be said by the above topological methods about systems which are substituted inside the rings because of inherent difficulties with parametrization of heteroatoms.

It is the purpose of this paper to demonstrate that some regularities can be derived but that no general prediction due to the number of π electrons can be made about the

---

[1] Garratt, P. J. "Aromaticity"; McGraw-Hill: London, 1971.

[2] Lewis, D.; Peters, D. "Facts and Theories of Aromaticity"; Macmillan: London, 1975.

[3] Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305.

[4] Gutman, I.; Milun, M.; Trinajstic, N. *MATCH* **1975**, *1*, 171; *J. Am. Chem. Soc.* **1977**, *99*, 1692.

[5] Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 6840; **1981**, *103*, 1633.

[6] Streitwieser, A. "A Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961; p 256 ff.

[7] Greenberg, A.; Tomkins, R. P. T.; Dobrovolny, M.; Liebman, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 6855.

0022-3263/84/1949-4475$01.50/0 © 1984 American Chemical Society

aromaticity of ring systems with unusual combinations of atoms. These systems have to be studied each one separately. In this fashion, we have found the smallest planar aromatic ring and the smallest nonplanar aromatic ring.

2. Three- and Four-Membered Rings with Two and Six π Electrons

The basis of this investigation is the aromaticity criterion recently proposed by the author.[8] A relation between the magnetic ring current and the weakest bond in the ring was proposed. The weakest bond was characterized by its bond order. It is not a π-electron bond order but the sum of σ and π contributions and can adjust to polarization both in the σ- and π-electron system. This is in line with the ab initio calculations by Lazzeretti et al.,[9] who observed that a substantial portion of the total magnetic susceptibility in benzene is due to σ bonding. But the relevant role of the π electrons cannot be dismissed. Substantial π bonding delocalized over the ring is a good basis for a ring current and its related aromaticity, whereas a pure σ bond poses a high resistance to a "flow" of π electrons so that no ring current will be observed. CC bond orders are 1.25 in ethane and 2.16 in ethylene.[8] We consider these as standard single and double bonds. From the calculation of more than 100 ring systems, it seemed suggestive to introduce the following ranges of aromaticity indexes for classification: (a) >1.60 highly aromatic, (b) 1.30–1.60 moderately aromatic, (c) 1.20–1.30 nonaromatic, (d) 1.10–1.20 moderately antiaromatic, (e) <1.10 highly antiaromatic. These ranges are not to be understood as perfectly rigid. A different parametrization may shift them somewhat, perhaps by ±0.05, but this is not drastic. Also, since the bond orders are rather insensitive to changes in bond lengths,[10] the conclusions drawn from SINDO1 calculations are not expected to be substantially modified if ab initio wave functions are used.

We have optimized the structures of selected three- and four-membered rings with two and six π electrons with the semiempirical MO method SINDO1.[11] This method was extensively tested and found superior to MINDO/3 and MNDO[12] in binding energies and geometries. The statistics show that SINDO1 is not only adequate for C, N and O but also for F, B, Be, and Li. This furnishes a basis for the present calculations on boron and beryllium compounds.

To simplify the issue we have not concentrated on molecules like cyclopropenone or methylenecyclopropene because of substitution effects. For completeness we report their aromaticity indexes as 1.39 and 1.38 which classify them as moderately aromatic, in line with ab initio calculations reported in ref 7. Rather we have taken systems without outer substitution so that no π electrons can be withdrawn or furnished from outside the ring. So the number of two and six π electrons is fixed in the ring. Table I presents bond orders and bond lengths, valencies, and charges of these molecules. The valencies were calculated according to recent definitions.[13,14]

Starting from the observation that cyclopropenyl cation $C_3H_3^+$ can be regarded as highly aromatic with an aromaticity index of 1.775 vs. 1.751 in benzene, we wanted to investigate how inner substitution of this system would modify the bond orders. A nonpolar analogue to $C_3H_3^+$ is N_3^+. We find that its aromaticity index of 1.856 is even higher than that in $C_3H_3^+$ or N_6.[7] So we think it would be the compound with the highest ring current. This does not mean increased thermodynamic stability. The N_3^+ ring should be much less stable than a localized reference structure. The situation is here similar to the one in N_6. If C^+ is replaced by B we obtain $BH(CH)_2$. Its aromaticity index of 1.614 qualifies it as highly aromatic. This conclusion was already reached by Schleyer et al.[15] who found that the stabilization of borirene, $BH(CH)_2$, due to π-electron delocalization amounts to 70% of that calculated for cyclopropenyl cation. Inner substitution of CH by N in this ring can lead to BHCHN with an index of 1.606, also highly aromatic. Alternatively BH can be formally replaced by Be which leads to $Be(CH)_2$ with an index of 1.565. We predict that its ring current properties would be similar to borazine, $B_3N_3H_6$, with an index of 1.528. $Be(CH)_2$ is the smallest aromatic ring to date, i.e., the ring with the smallest number of electrons. The existence of such a ring is supported by unpublished ab initio HF 6-31G* calculations by Kos and Schleyer,[16] who found the following ring geometry: BeC = 1.553 Å, CC = 1.373 Å. Most interestingly they find $Be(CH)_2$ to be 15.3 kcal/mol more stable than Be + C_2H_2. The relative stability is 22.9 kcal/mol in a MP2/6-31G* calculation. Previously Swope and Schaefer[17] had found a repulsive interaction of Be with

Table I. Three- and Four-Membered Rings with Two and Six π Electrons (Aromaticity Index with Asterisk)

molecule	bond	bond order	bond length (Å)	atom	valence	charge
N_3^+	NN	1.856*	1.255	N	2.82	0.33
$BH(CH)_2$	BC	1.614*	1.490	B	3.50	0.13
	CC	1.899	1.352	C	3.87	−0.08
BHCHN	BC	1.606*	1.478	B	3.45	0.20
	BN	1.648	1.412	C	3.81	0.01
	CN	1.941	1.284	N	2.89	−0.17
$Be(CH)_2$	BeC	1.565*	1.602	Be	2.56	0.19
	CC	1.836	1.376	C	3.85	−0.12
$(BH)_2NH$	BB	1.347*	1.645	B	3.38	0.17
	BN	1.636	1.410	N	3.51	−0.29
BeC_2	BeC	1.248*	1.638	Be	2.21	0.43
	CC	2.439	1.277	C	3.20	−0.22
BeB_2	BeB	1.066*	1.760	Be	2.50	0.09
	BB	1.322	1.545	B	3.07	−0.05
$(BH)_2C$	BB	0.899*	1.982	B	3.37	0.28
	BC	2.059	1.390	C	3.54	−0.40
Be_2C	BeBe	0.746*	2.235	Be	2.35	0.25
	BeC	1.674	1.505	C	3.71	−0.49
$C_4H_4^{2+}$	CC	1.626*	1.418	C	3.69	0.23
	CC[a]	0.579	1.858			
$(BHCH)_2$	BC	1.548*	1.518	B	3.43	0.23
	BB[a]	0.346	2.191	C	3.83	−0.17
	CC[a]	0.804	1.747			
$(BeCH)_2$	BeC	1.533*	1.637	Be	2.54	0.22
	BeBe[a]	0.308	2.335	C	3.72	−0.25
	CC[a]	0.548	2.146			
$(BH)_2(CH)_2$	BB	1.219*	1.690	B	3.28	0.12
	BC	1.385	1.554	C	3.89	−0.02
	CC	1.829	1.366			
$(CH)_2(NH)_2$	NN	1.059*	1.439	C	3.94	0.07
	CN	1.180	1.455	N	3.03	−0.06
	CC	1.964	1.359			
$(CHNH)_2$	CN	1.396*	1.416	C	3.57	0.12
	CC[a]	−0.417	1.947	N	3.34	−0.14
	NN[a]	−0.286	1.972			

[a] Diagonal bonds.

---

[8] Jug, K. *J. Org. Chem.* **1983**, *48*, 1344.

[9] Lazzeretti, P.; Zanasi, R. *J. Chem. Phys.* **1981**, *75*, 5019. Lazzeretti, P.; Rossi, E.; Zanasi, R. *J. Chem. Phys.* **1982**, *77*, 3129.

[10] Jug, K. *Croat. Chem. Acta*, in press.

[11] Nanda, D. N.; Jug, K. *Theoret. Chim. Acta* **1980**, *57*, 95.

[12] Jug, K.; Nanda, D. N. *Theoret. Chim. Acta* **1980**, *57*, 107, 131.

[13] Gopinathan, M. S.; Jug, K. *Theoret. Chim. Acta* **1983**, *63*, 497, 511.

[14] Jug, K. *J. Comput. Chem.*, in press.

[15] Krogh-Jespersen, K.; Cremer, D.; Dill, J. D.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 2589.

[16] Schleyer, P. v. R., private communication.

C_2H_2. This is obviously due to their frozen geometry of acetylene. In all of these systems two atoms furnished one π electron each to the π-electron system. If one atom furnishes two electrons, the aromaticity is greatly reduced because the polarity of the bonds can no longer be overcome so easily as in previous systems. An example is $(BH)_2NH$ which is only slightly aromatic with an index of 1.347. It is interesting to note that the difference between BHCHN and $(BH)_2NH$ is similar to the difference between pyridine (1.731) and pyrrole (1.423).[8] The pyridinic nitrogen with one π electron allows a much better ring current than the pyrrolic nitrogen with two π electrons because the potential of the latter nitrogen core is more attractive. Further examples for system with two π electrons from one atom are $(BH)_2C$ with an index of 0.899 and Be_2C with an index of 0.746. Both systems should be antiaromatic even more than cyclobutadiene with an index of 0.98.[8] This result is related to the fact that the BB and BeBe bonds are very weak and quite long. The final two three-membered rings are BeC_2 and BeB_2. The in-plane bent bond contribution to the total BeC bond is 0.68 in BeC_2, whereas it is only 0.47 in BeB_2. The increase in the bond order is due to an additional bonding orbital in BeC_2. If we compare BeC_2 with $Be(CH)_2$ the same conclusion holds, namely, another occupied MO contributes to a further increase in the bent bond portion of BeC bond order in $Be(CH)_2$ and yields 1.02 as the total in-plane bond order. All three systems have almost equal out-of-plane π-bond orders: 0.60 in BeB_2, 0.57 in BeC_2, and 0.54 in $Be(CH)_2$. The out-of-plane π bond in BeB_2 seems surprising. But despite its presence and magnitude, the weak σ bond is responsible for the antiaromatic character of this molecule. Ab initio calculations on Be_2C and BeC_2 have been recently performed by Frenking.[18]

Our interest in the four-membered rings with two π electrons originated from the work of Schleyer and collaborators who had found by means of ab initio calculations with various basis sets (STO-3G, 4-31G, 6-31G*) a nonplanar cyclobutadiene dication[15,19] and a nonplanar 1,3-diboretene.[15] They found the following resonance energies: 18.6 kcal/mol for $C_4H_4^{2+}$, 14 kcal/mol for $(BHCH)_2$, and 26.9 kcal/mol for 1,2-diboretene $(BH)_2(CH)_2$. They concluded that all three compounds are aromatic. They find that relief of the repulsive 1,3 cross-ring interactions in $C_4H_4^{2+}$ and $(BHCH)_2$ are responsible for these violations of the general expectation that aromatic molecules will prefer planarity. Our calculations of these compounds with SINDO1 gave the following results.

From the four-membered rings with two π electrons $(BH)_2(CH)_2$ is planar and has C_{2v} symmetry. It would have to be classified as nonaromatic due to its weak BB bond with a bond order of 1.219. $(BHCH)_2$ is nonplanar with C_{2v} symmetry. We find a puckering angle of 56.1°. The system is aromatic with an aromaticity index of 1.548.

This aromaticity originates from two sources. There is substantial delocalization in the π system with an out-of-plane π bond order of 0.43 and also increased in-plane π bonding with a bond order contribution of 0.29. With the terms in-plane and out-of-plane π bonding we refer to each of the two planes containing three ring atoms. Since bond orders are not exclusive, i.e., not additive, the π MO's of the ring bond can serve to some extent to establish nonnegligible σ bond orders for the diagonal bonds. This is not necessarily in disagreement with Schleyer's statement[15] that the negative overlap charge is reduced by the folding of this ring. Overlap charge does not arise in our orthogonalized MO method SINDO1, so the criteria of overlap charge and bond order are not directly comparable. The trend is the same in both cases, namely, the diagonal σ bonding is enhanced by folding. The situation is similar in $C_4H_4^{2+}$ which is nonplanar with D_{2d} symmetry and a puckering angle of 59.6°. Its aromaticity index is 1.63, whereas the planar form has an index of 1.51. Here again folding is accompanied not only with increased in-plane bond orders for adjacent ring bonds but also with slightly increased diagonal σ bond orders and reduced out-of-plane diagonal π bond orders.

It is gratifying to see that our structural data are close to the ab initio data. Ab initio bond lengths are 1.477 Å (STO-3G) and 1.510 (4-31G) in $(BHCH)_2$ compared to our 1.548 Å and 1.457 Å (STO-3G) and 1.431 Å (4-31G) in $C_4H_4^{2+}$ compared to our 1.418 Å. The ab initio puckering angles are somewhat smaller than ours: 54.9° (STO-3G), 48.2° (4-31G) in $(BHCH)_2$ and 33.2° (STO-3G), 35.8° (4-31G), and 42.6° (6-31G*) in $C_4H_4^{2+}$.[15]

We also agree with their conclusion of stability, i.e., $(BHCH)_2$ is more stable than $(BH)_2(CH)_2$. But we emphasize that we find the latter compound nonaromatic because of insufficient BB bonding. The larger resonance energy of 27 kcal/mol in $(BH)_2(CH)_2$ compared to 14 kcal/mol in $(BHCH)_2$ of Schleyer's 6-31G* calculation[15] may be partly an artifact arising from the molecules used for the actual energy comparison. There is an indication to this extent in ref 15. After completion of this work we learned that extensive experimental work was in progress on the elusive diboretenes which has come to fruition. The first syntheses of diboretene derivatives were achieved in three different laboratories.[20-22] Siebert's[22] puckered structure of $(BXCY)_2$ with $X = N(CH_3)_2$ and $Y = C(CH_3)_3$ gave an experimental CC distance of 1.81 Å compared to Schleyer's 1.86 Å and our 1.75 Å in the unsubstituted compound. The latest on this matter is a calculation of Schleyer and Budzelaar[23] who find the bicyclobutane-2,4-dione also folded.

It seemed only natural to look for the smallest nonplanar aromatic compound. $(BeCH)_2$ seemed to be a good choice. We find this molecule folded with a puckering angle of 40.7°. Its aromaticity index of 1.533 classifies it as moderately aromatic similar to $(BHCH)_2$. But the CC distance of 2.15 Å is much longer than in the former case because we find the ring bond length with 1.64 Å much longer than the BC ring bond length.

An investigation of the aromaticity of four-membered rings with six π electrons found the $C_4H_4^{2-}$ anion moderately aromatic with an index of 1.510. It is now important to notice that substitution of two CH^- by two NH creates a situation similar to the one for the boron compounds. For the C_s structure of $(CH)_2(NH)_2$ the NN bond is weaker than a single bond with a bond order of 1.025. The compound must be classified as antiaromatic. The π electrons of the pyrrolic nitrogens are barely delocalized. This results in the cancellation of π bonding of the bonding π MO by an antibonding π MO. The latter has a node in the NN bond.

---

(17) Swope, W. C.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1976**, *98*, 7962.

(18) Frenking, G. 19. Symposium für Theoretische Chemie, Oct 3–7, 1983, Mülheim.

(19) Krogh-Jespersen, K.; Schleyer, P. v. R.; Pople, J. A.; Cremer, D. *J. Am. Chem. Soc.* **1978**, *100*, 4301. Chandrasekhar, J.; Schleyer, P. v. R.; Krogh-Jespersen, K. *J. Comput. Chem.* **1981**, *2*, 356.

(20) van der Kerk, S. M.; Budzelaar, P. H. M.; van der Kerk-van Hoof, A.; van der Kerk, G. J. M.; Schleyer, P. v. R. *Angew. Chem.* **1983**, *95*, 61.

(21) Wehrmann, R.; Pues, C.; Klusik, H.; Berndt, A. *Angew. Chem.* **1984**, *96*, 372.

(22) Hildenbrand, M.; Pritzkow, H.; Zemek, U.; Siebert, W. *Angew. Chem.* **1984**, *96*, 371.

(23) Schleyer, P. v. R.; Budzelaar, P. H. M. *Angew. Chem.*, in press.

Table II. Eight-Membered Rings with Six and Ten π Electrons (Aromaticity Index with Asterisk)

molecule	bond	bond order	bond length	atom	valence	charge
$C_8H_8^{2-}$	CC	1.695	1.432	C	3.89	−0.09
$BC_2BC_4H_8$	BC_1	1.372*	1.573	B	3.27	0.33
	C_4C_5	1.381	1.488	C_1	3.95	−0.07
	BC_6	1.410	1.563	C_5	3.97	0.11
	C_1C_2	2.006	1.349	C_6	3.95	−0.16
	C_5C_6	2.007	1.358			
$NC_2NC_4H_8$	NC_1	1.330*	1.419	N	3.24	−0.22
	C_4C_5	1.404	1.475	C_1	3.94	0.11
	NC_6	1.372	1.410	C_5	3.97	0.06
	C_1C_2	2.003	1.368	C_6	3.94	0.20
	C_5C_6	1.998	1.368			
$NC_2OC_4H_7$	NC_1	1.335	1.409	N	3.23	−0.21
	C_4C_5	1.373	1.488	C_1	3.94	0.10
	NC_6	1.364	1.411	C_5	3.97	−0.06
	C_1C_2	2.006	1.363	C_6	3.94	0.19
	C_5C_6	2.013	1.355	O	2.27	−0.22
	OC_2	1.333*	1.376	C_2	3.92	0.15
	OC_3	1.383	1.366	C_3	3.92	0.24
	C_3C_4	2.013	1.350	C_4	3.97	−0.08
$NC_2OC_4H_6X^a$	NC_1	1.239*	1.466	N	3.15	0.22
	C_4C_5	1.389	1.460	C_1	3.94	0.03
	NC_6	1.289	1.439	C_5	3.98	−0.02
	C_1C_2	2.020	1.376	C_6	3.95	0.14
	C_5C_6	2.026	1.356	O	2.27	0.22
	OC_2	1.338	1.383	C_2	3.92	0.19
	OC_3	1.374	1.368	C_3	3.92	0.25
	C_3C_4	2.011	1.356	C_4	3.97	−0.09
$OC_2OC_4H_6$	OC_1	1.331*	1.388	O	2.27	−0.21
	C_4C_5	1.390	1.476	C_1	3.92	0.13
	NC_6	1.384	1.370	C_5	3.96	−0.07
	C_1C_2	2.008	1.380	C_6	3.92	0.24
	C_5C_6	2.009	1.368			

[a] $X = COOCH_3$.

For the alternating ring $(CHNH)_2$ we obtain again a nonplanar compound of C_{2v} symmetry with a dihedral angle of 32.3°. It is moderately aromatic with an index of 1.395, less than in pyrrole. Here alternation does not allow diagonal bonding, rather the N atom seeks the usual pyramidal form of bonding. The CC bond order is −0.42 and the NN bond order −0.29.

Charge does not characterize aromaticity. But we find hypervalent beryllium, boron, pyrrolic nitrogen, and subvalent pyridinic nitrogen in the aromatic compounds. This refers to the normal valencies of 2 for Be and 3 for B and N. Subvalent atoms have lower, hypervalent atoms higher values than these reference values. This trend to subvalent and hypervalent atoms in a ring serves to delocalize the π electrons in order to create a uniform distribution of covalent bond sharing and to sustain a ring current.

3. Eight-Membered Rings with Six and Ten π Electrons

In Table II we present the properties of eight-membered rings upon inner and outer substitution. It is generally agreed that $C_8H_8^{2-}$ can be considered as aromatic. We find equal bond lengths and bond orders and an aromaticity index of 1.695 close to benzene on the basis of SINDO1 optimization. Formal 1,4-substitution of C^- by B and CH^- by NH and O results in significant changes. All systems are practically planar but highly localized. The two carbon atoms C_1 and C_2 between the two heteroatoms form a double bond with a bond order of approximately 2 compared to a standard double bond with bond order of 2.15. The bond orders of bonds involving the heteroatoms are the weakest links in the ring. The boron compound with six π electrons is moderately aromatic with the smallest bond order 1.372. We find the unsubstituted nitrogen and oxygen compounds with ten π electrons slightly less aromatic with indexes of 1.33. Finally the outside substituted nitrogen oxygen compound with the electron-withdrawing group $COOCH_3$ is clearly nonaromatic with an index of 1.24. With a more limited geometry optimization, a value of 1.30 was initially obtained. So the indexes depend on the degree of geometry optimization, which must be done with much care.

Experimental work by Prinzbach et al.[24-26] and Vogel et al.[27] found the structure of these eight-membered rings dependent on the kind of substituent. They found planar forms for donor-substituted derivatives and mobile twist-boat-chair conformations for acceptor-substituted derivatives. Our results agree with Prinzbach's conclusions. Although aromaticity indexes of 1.33 for the unsubstituted compounds are not substantially above the threshold for a ring current, there is a major difference to the nonaromatic acceptor-substituted compound with group $COOCH_3$. In the latter molecule there is a pronounced tendency to nonplanarity with a NCCO dihedral angle of 8° whereas we find the unsubstituted compounds planar. Since the systems with ten π electrons considered here are analogues of pyrrole and furan, we expect them to be less aromatic than either of these. The core potential hinders the delocalization and prevents a ring current similar to pyridine and related compounds. To reinforce π-electron delocalization in such eight-membered rings, strong donor substituents are needed. The size of such substituents[28] is beyond the scope of this paper and the present computational capabilities of our program.

In summary, we conclude that inner substitution causes usually a much more drastic change in the ring than an outer substitution. But strong donor or acceptor molecules as substituents have a definitive influence on the aromaticity of a ring.

Acknowledgment. I thank Prof. H. Prinzbach for drawing my attention to the eight-membered rings and for structural data prior to publication and Prof. P. v. R. Schleyer for supplying theoretical and experimental data on some of the three- and four-membered rings.

Registry No. N_3^+, 92220-05-8; $BH(CH)_2$, 16488-40-7; BHCHN, 92220-01-4; $Be(CH)_2$, 92219-99-3; $(BH)_2NH$, 85302-95-0; BeC_2, 12070-28-9; BeB_2, 12228-40-9; $(BH)_2C$, 92220-02-5; Be_2C, 506-66-1; $C_4H_4^{2+}$, 12240-33-4; $(BHCH)_2$, 90171-84-9; $(BeCH)_2$, 92220-00-3; $(BH)_2(CH)_2$, 77385-68-3; $(CH)_2(NH)_2$, 5687-03-6; $(CHNH)_2$, 92220-03-6; $C_8H_8^{2-}$, 34510-09-3; $BC_2BC_4H_8$, 92220-04-7; $NC_2NC_4H_8$, 56039-49-7; $NC_2OC_4H_7$, 30318-11-7; $NC_2OC_4H_6CO_2Me$, 89462-59-9; $OC_2OC_4H_6$, 292-88-6.

---

(24) Prinzbach, H.; Müller, K. H.; Kaiser, C.; Hunkler, D. *Tetrahedron Lett.* **1980**, *21*, 3475.

(25) Breuninger, M.; Schwesinger, R.; Gallenkamp, B.; Müller, K. H.; Fritz, H.; Hunkler, D.; Prinzbach, H. *Chem. Ber.* **1980**, *113*, 3161.

(26) Breuninger, M.; Gallenkamp, B.; Müller, K. H.; Fritz, H.; Prinzbach, H.; Daly, J. J.; Schönholzer, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 964.

(27) Altenbach, H. J.; Stegelmeier, H.; Wilhelm, M.; Voss, B.; Lex, J.; Vogel, E. *Angew. Chem.* **1979**, *91*, 1028; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 962.

(28) Zipperer, B.; Hunkler, D.; Fritz, H.; Rihs, G.; Prinzbach, H. *Angew. Chem.* **1984**, *96*, 296.