with 0.5% acetone in dichloromethane afforded 13.7 mg (32%) of the desired dyad. The free amino group of the dyad was acetylated to yield **5** by simply dissolving the aminodyad in 2 mL of acetic anhydride and five drops of pyridine. The mixture was allowed to stand for 1 h. Following dilution with chloroform, extraction with a saturated solution of sodium bicarbonate, two extractions with water, and evaporation of the solvents at reduced pressure, the residue was purified by column chromatography on silica gel with chloroform to yield quantitatively diporphyrin **5**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.85–9.01 (16 H, m, pyrrole-H), 8.49 (1 H, s, 5Ar-NH), 8.45 (4 H, AB, J = 8.2 Hz, 5Ar2-H, 3-H, 5-H and 6-H), 8.33 (2 H, d, J = 8.4 Hz, 5′Ar2-H and 6-H), 8.20 (2 H, d, J = 8.4 Hz, 5′Ar3-H and 5-H), 8.17 (2 H, d, J = 8.2 Hz, 15Ar2-H and 6-H), 7.88 (2 H, d, J = 8.2 Hz, 15Ar3-H and 5-H), 8.11 (4 H, d, J = 7.9 Hz, 10, 20Ar2-H and 6-H), 7.57 (4 H, d, J = 7.9 Hz, 10,20Ar3-H and 5-H), 7.46 (1 H, s, 15Ar-NH), 2.72 (6 H, s, Ar-CH$_3$), 2.35 (3 H, s, COCH$_3$), −2.72 (2 H, s, NH′), −2.81 (2 H, s, NH); UV–vis absorption (dichloromethane) λ_{max} (nm) 420, 512, 554, 590, 650; fluorescence emission (λ_{ex} = 590 nm in dichloromethane) λ_{max} (nm) 655, 718.

Diporphyrin 6. Freshly prepared acid chloride **18** (from 30 mg (0.032 mmol) of the acid) was dissolved in 10 mL of toluene, and the resulting solution was added to 8.0 mg (0.012 mmol) of **19** dissolved in a mixture of toluene (2 mL) and pyridine (0.5 mL). The mixture was stirred for 5 h, and the solvent was then distilled at reduced pressure. The residue was dissolved in water and dichloromethane and extracted with dichloromethane. The organic layer was evaporated to dryness, the residue dissolved in toluene, and the resulting solution distilled to remove any residual water and pyridine. The residue was purified by chromatography on silica gel (dichloromethane) and recrystallization from dichloromethane and methanol to give 18 mg of compound **6** (95% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.88–9.01 (16 H, m, pyrrole-H), 8.50 (1 H, s, 5Ar-NH), 8.46 (2 H, AB, J = 9.0 Hz, 5Ar3-H, and 5-H), 8.47 (2 H, AB J = 9.0 Hz, 5Ar2-H and 6-H), 8.34 (2 H, d, J = 8.4 Hz, 5′Ar3-H and 5-H), 8.22 (2 H, d, J = 8.4 Hz, 5′Ar2-H and 6-H), 8.13 (4 H, d, J = 7.6 Hz, 10,20Ar2-H and 6-H), 8.11 (2 H, d, J = 7.0 Hz, 15Ar2-H and 6-H), 7.58 (4 H, d, J = 7.6 Hz, 10,20Ar3-H and 5-H), 7.56 (2 H, d, J = 7.0 Hz, 15Ar3-H and 5-H), 2.72 (6 H, s, 10,20Ar-CH$_3$), 2.71 (3 H, s, 10,15,20Ar-CH$_3$), −2.87 (2 H, s, pyrrole-NH), −2.78 (2 H, s, PF15 pyrrole-NH); UV–vis absorption (dichloromethane) λ_{max} (nm), 420, 514, 552, 590, 648; fluorescence emission (λ_{ex} = 590 nm, dichloromethane) λ_{max} (nm), 652, 718.

Zinc 5-(4-Aminophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (20) was prepared from 15 mg (0.022 mmol) of **19** via the method described for **10**. The yield was 14 mg (86%): UV–vis absorption (dichloromethane) λ_{max} (nm) 422, 550, 590; fluorescence emission (λ_{ex} = 550 nm in dichloromethane) λ_{max} (nm) 603, 649.

Diporphyrin 7. Freshly prepared acid chloride **18** (from 20 mg (0.022 mmol) of the acid) was dissolved in 10 mL of toluene, and the resulting solution was added to 7.4 mg (0.010 mmol) of **20** dissolved in a mixture of toluene (2 mL) and pyridine (2 mL). The mixture was stirred for 14 h, and the solvents were then evaporated at reduced pressure. The residue was dissolved in dichloromethane and extracted with water. The organic layer was evaporated to dryness, the residue dissolved in toluene, and the resulting solution distilled to remove any residual water and pyridine. The residue was purified by chromatography on silica gel (dichloromethane) and recrystallization from dichloromethane and methanol to give 9.0 mg of **7** (54% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.95–9.02 (16 H, m, pyrrole-H), 8.50 (1 H, s, 5Ar-NH), 8.46 (2 H, AB, J = 9.0 Hz, 5Ar3-H, and 5-H), 8.47 (2 H, AB, J = 9.0 Hz, 5Ar2-H and 6-H), 8.34 (2 H, d, J = 8.4 Hz, 5′Ar3-H and 5-H), 8.22 (2 H, d, J = 8.4 Hz, 5′Ar2-H and 6-H), 8.13 (4 H, d, J = 7.6 Hz, 10,20Ar2-H and 6-H), 8.11 (2 H, d, J = 7.0 Hz, 15Ar2-H and 6-H), 7.58 (4 H, d, J = 7.6 Hz, 10,20Ar3-H and 5-H), 7.56 (2 H, d, J = 7.0 Hz, 15Ar3-H and 5-H), 2.72 (6 H, s, 10,20Ar-CH$_3$), 2.71 (3 H, s, 15Ar-CH$_3$), −2.78 (2 H, s, PF15 pyrrole-NH); UV–vis absorption (dichloromethane) λ_{max} (nm), 422, 510, 550, 588, 640; fluorescence emission (λ_{ex} = 550 nm, dichloromethane) λ_{max} (nm), 600, 643, 710.

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Tetramethylene Dications $(CH_2)_4{}^{2+}$: Are the Norbornadiene Dication, the Pagodane Dication, and Related Systems Aromatic?[‖]

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Contribution from the Institut für Organische Chemie der Friedrich-Alexander, Universität Erlangen-Nürnberg, 8520 Erlangen, West Germany, Bayer AG, Zentrale Forschung und Entwicklung, 5090 Leverkusen, West Germany, and Institut für Organische Chemie und Biochemie der Universität Freiburg, Freiburg, West Germany. *Received January 3, 1990*

Abstract: The $(CH_2)_4{}^{2+}$ potential energy hypersurface has been investigated by semiempirical and ab initio calculations. The global minimum is an acyclic structure of C_i symmetry. Harmonic vibrational analysis of the rectangular cyclobutane dication (D_{2h}), which serves as a model for "σ-aromatic" pagodane and norbornadiene dications, indicates three imaginary frequencies. Nonetheless, strong evidence that the pagodane dication has a nonclassical, "aromatic" structure of D_{2h} symmetry is presented. A rapid equilibrium of two classical C_{2v} structures and a diradical D_{2h} species, in which both are consistent with the experimental NMR spectroscopic data, can be excluded on the basis of our theoretical investigations. The norbornadiene dication is also predicted to be stabilized by aromaticity, whereas structures with larger distances between the two formal ethylene radical cations are predicted to exhibit increasing diradicaloid character.

Treated at −80 °C with SbF$_5$/SO$_2$ClF, [1.1.1.1]pagodane (**1**) is oxidized to give a dication persistent for several hours at room temperature.[1] This behavior is remarkable since no stabilizing aromatic or heteroatomic substituents are present. ^{13}C and ^{1}H NMR spectra indicate the preservation of the original D_{2h} symmetry at least on the observational time scale. Quenching **1** with methanol yields the decacyclic derivative **2**. The remarkable stability of the dication implies an extraordinary electronic

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[‖] Dedicated to H. Prinzbach on the occasion of his 60th birthday.

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(1) (a) Prakash, G. K. S.; Krishnamurthy, V. V.; Herges, R.; Bau, R.; Yuan, H.; Olah, G. A.; Fessner, W.-D.; Prinzbach, H. *J. Am. Chem. Soc.* **1986**, *108*, 836. (b) For review on organic dications, see: Lammertsma, K.; Schleyer, P. v. R.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *10*, 1321.

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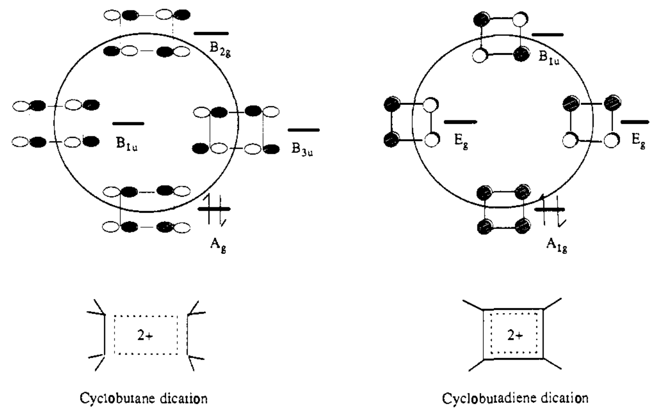
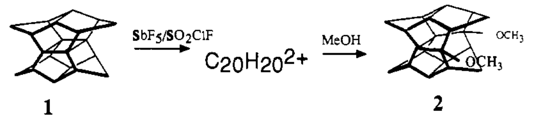
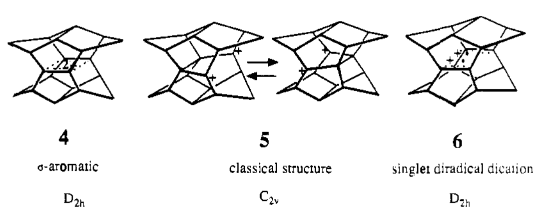


Figure 1. Corresponding orbitals of the cyclobutane and the cyclobutadiene dications. These are represented in idealized rectangular (D_{2h}) and square (D_{4h}) symmetries, even though other forms are more stable.[21a]

structure. To account for the experimental facts, a σ-aromatic formulation **4**, rather than a set of equilibrating classical species **5**, was proposed.[1,2]

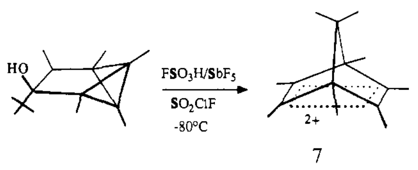




In the present context, "σ-aromatic" implies significant overlap between the orbitals on the more distant carbons of **4**. This is illustrated in Figure 1 for the parent system, the cyclobutane dication. The orbitals shown are topologically equivalent to those for the cyclobutadiene dications. In both cases, formal interactions between two olefin radical cation moieties are involved. If the separation is large, as in **6**, no significant stabilization due to such interactions can be expected.

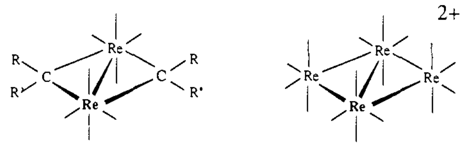
MNDO calculations indicated both the D_{2h} structure **4** and the C_{2v} structure **5** to be minima on the energy hypersurface, the "aromatic" structure being 4 kcal/mol more stable than its classical counterpart.[2] These theoretical results have been interpreted as a further support for the D_{2h} structure.[2] Although the available evidence seems to favor the aromatic structure **4**, neither a fast equilibrium of classical C_{2v} structures **5** nor a singlet diradical dication **6** can be excluded. Indeed, the MNDO geometry of **4** would be consistent with the latter. The longer bond distance in the central four-membered ring in **4** was calculated to be 2.592 Å. Through space interactions over such a distance should be extremely weak, the contraction of the radial extension of the orbitals caused by the positive charge should further weaken the interaction between the two formal ethylene radical cation units. The pagodane dication is not the first dication for which a σ-aromatic structure was proposed. In 1981, Hogeveen and coworkers[3] synthesized the octamethylnorbornadiene dication via ionization and rearrangement of a tricyclic alcohol. On the basis of their NMR and quenching results, they proposed the structure **7**.

Dication **7** is stable up to −40 °C in magic acid solution. The appearance of only one signal in the ^{1}H NMR spectrum (δ 2.47) and only two ^{13}C signals (δ 151.7, singlet, and δ 16.9, quartet) even at low temperatures was explained by fast methyl and skeleton carbon scramblings.

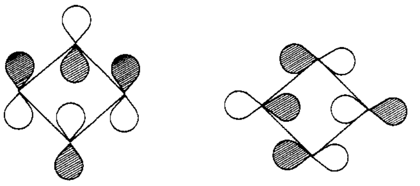


While the geometries, electronic structures, and the stabilities ("aromaticity") of these pagodane (**4**) and norbornadiene (**7**) dications are intriguing problems themselves, they are part of a more general picture.

Tetramethylene dications $(CH_2)_4^{2+}$ and their derivatives are of interest in other contexts as well. In his Noble Prize lecture, ***Building Bridges Between Inorganic and Organic Chemistry***, R. Hoffmann described numerous isolobal analogies,[4] e.g.

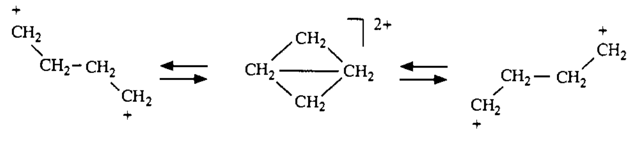


He then extended the same reasoning; "It is interesting to speculate when we might see the missing members of the series on the organic side, $(CO)_4Re(CH_3)_3$ and $(CH_2)_4^{2+}$". Implied is structure **9** (Figure 2) for the cyclobutane dication. Hoffmann's cyclic $(CH_2)_4^{2+}$ structure **9** seems peculiar at first sight because of the "extra" transannular bond. At the time of Hoffmann's address, we had already been concerned with the question of what happens structurally when two electrons are removed from a saturated hydrocarbon. For example, in one of the states of triplet $C_2H_6^{2+}$, extra C–C bonding results when two valence electrons are removed from the degenerate higher lying orbitals with C–C antibonding character.[5] Structure **9** can be understood similarly. The cyclobutane HOMO's are a doubly degenerate set of Walsh-type orbitals of π*-symmetry:



If two electrons are lost from one of these orbitals to give a singlet cyclobutane dication, one of the repulsive transannular interactions should be relieved and the distortion implied by structure **9** should result. Alternatively, the rhombic structure **9** could be viewed as a transition state for a possible dyotropic rearrangement[6] of an open dication **8**.

Similar doubly bridged arrangements have been found in dilithioacetylene,[6b] dilithioethylene,[7] and dilithioethane.[8]



Computational Methods

Semiempirical calculations (MINDO/3, MNDO, AM1) were performed with the AMPAC program package[9] and ab initio calculations of

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[2] (a) Prakash, G. K. S.; Krishnamurthy, V. V.; Herges, R.; Bau, R.; Yuan, H.; Olah, G. A.; Fessner, W.-D.; Prinzbach, H. *J. Am. Chem. Soc.* **1988**, *110*, 7764. (b) Fessner, W.-D.; Prinzbach, H. 12th Austin Symposium on Molecular Structure, Austin, TX, 1988, 26.

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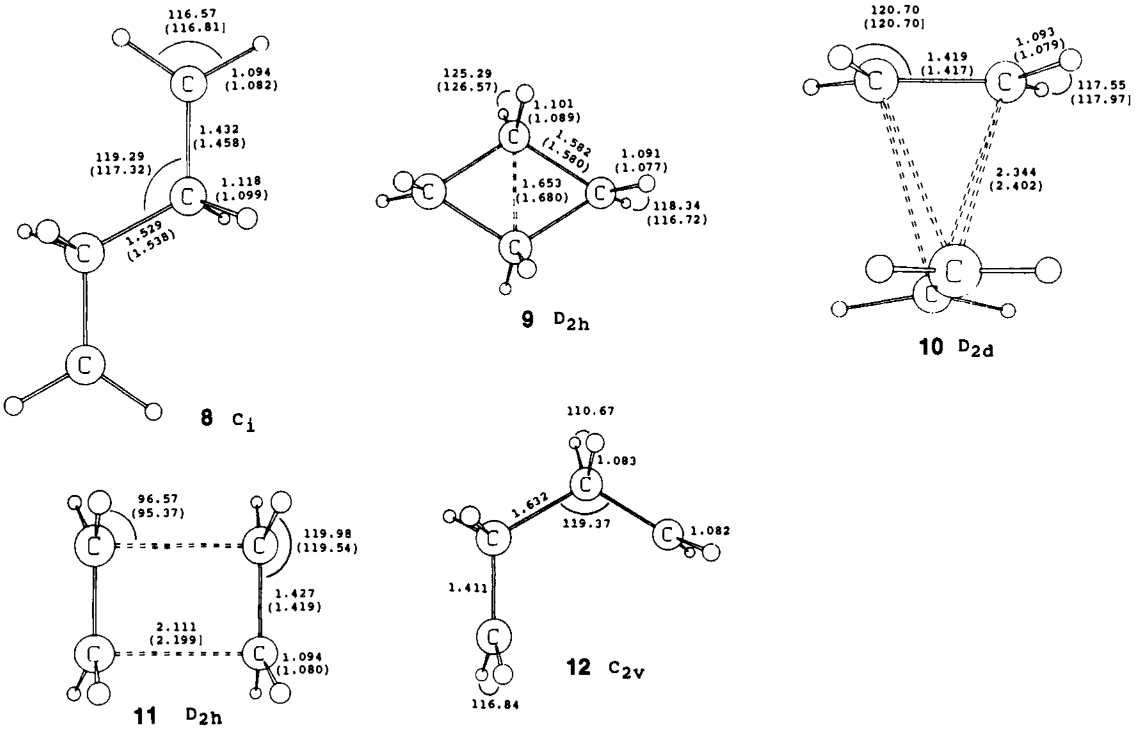

Figure 2. Geometries of five different $(CH_2)_4^{2+}$ structures optimized at the MP2/6-31G* level (6-31G* geometries in parentheses).

Table I. Relative Energies of $(CH_2)_4^{2+}$ Structures[a]

compd	MNDO	3-21G// 3-21G	6-31G*// 6-31G*	MP2/ 6-31G*// 6-31G*	MP2/ 6-31G*// MP2FULL/ 6-31G*	MP3/ 6-31G*// MP2FULL/ 6-31G*	MP4SDTQ/ 6-31G*// MP2FULL/ 6-31G*
8 (C_i)	0.0	0.0 (0)	0.0 (0)	0.0	0.0 (0)	0.0	0.0
9 (D_{2h})	75.6	60.9 (1)	53.5 (1)	14.9	15.4 (2)	25.8	31.9
10 (D_{2d})	76.5	34.6 (3)	37.0 (3)	25.8	26.2 (3)	29.2	37.1
11 (D_{2h})	66.2	28.8 (3)	34.4 (3)	22.1	22.2 (2)	25.8	33.7
12 (C_{2v})	19.7	25.5 (3)	24.1 (3)	25.3	*b*	*b*	*b*

[a] Energies in kilocalories per mole. The number of imaginary frequencies is given in parentheses. [b] Gives 11; see text.

the $(CH_2)_4^{2+}$ structures with the GAUSSIAN88[10] package using the standard basis sets and post SCF treatments.[11] The pagodane dications **4** and **5** the norbornadienyl dication **13**, and the tricyclic dications **14** and **15** were optimized with CADPAC.[12] Harmonic vibration frequency modes were calculated with the analytic gradient methods implemented in CADPAC. MC-SCF calculations were performed with the GAMESS program.[13] Reference states were selected according to the CI eigenvector of a MNDO full CI calculation using all states with coefficients greater than 0.025. ^{13}C-shift calculations were computed with IGLO[14] with double-ζ (DZ) basis sets.

Energy and Structure of $(CH_2)_4^{2+}$ Isomers

Tetramethylene cations $(CH_2)_4^{2+}$ can be viewed as model compounds of pagodane and norbornadienyl dication as well as those of the rhombic structure **9** and its isolobal analogues. In order to gain further insight in the electronic structures and relative stabilities, we carried out extensive investigations of the $(CH_2)_4^{2+}$ potential energy hypersurface at semiempirical and lower ab initio levels. Five species were selected as being of primary interest, and the geometries were reoptimized at MP2(FULL)/6-31G*, i.e., including correlation corrections of the second order of perturbation theory on a split valence basis set augmented by polarization functions on carbon (Figure 3). Structures **5**, **8**, and **12** are representatives of open 1,4-butadiyl dications; **9** and **11** are the two D_{2h} dications expected from removal of two electrons from cyclobutane. Alternatively, **9** can be viewed as the possible dyotropic rearrangement transition state of **8** and **11** as a complex between two ethylene radical cations. Another possible combi-

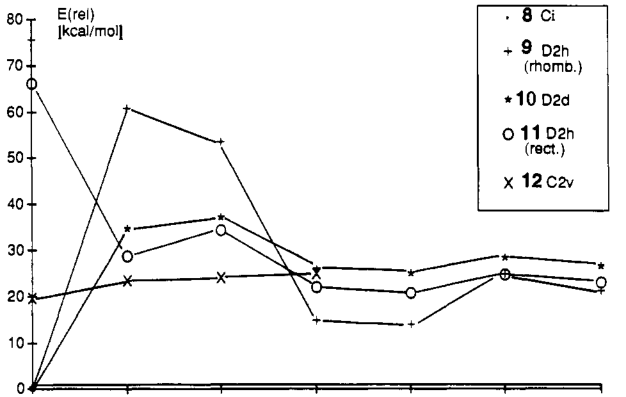

Figure 3. Relative energies of five different $(CH_2)_4^{2+}$ structures at various levels of theory. The values are based on the global minimum of C_i symmetry.

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Table II. Energies[a] of 4 and 5, Calculated with MINDO/3, MNDO, AM1 and ab Initio 3-21G//3-21G, and MP2/3-21G//3-21G

	MINDO/3 ΔH_f (kcal/mol)	MNDO ΔHf (kcal/mol)	AM1 ΔH_f (kcal/mol)	3-21G//3-21G hartree/particle	MP2/3-21G// 3-21G hartree/particle
4 D_{2h}	617.27	559.51	523.69	−764.1552	−765.7838
5 C_{2v}	*b*	563.54	*b*	*b*	

[a] All stationary points were confirmed to be minima by harmonic frequency analysis. [b] Closes to rectangular structure **4** upon optimization.

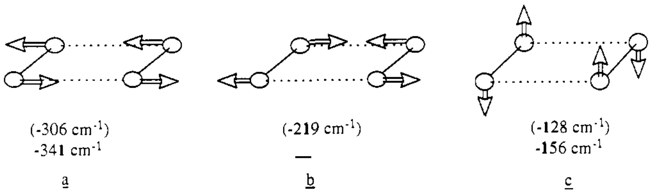


Figure 4. Frequency modes of **11**; MP2/6-31G* optimized structure (6-31G* values in parentheses). Only modes of carbon atoms are shown.

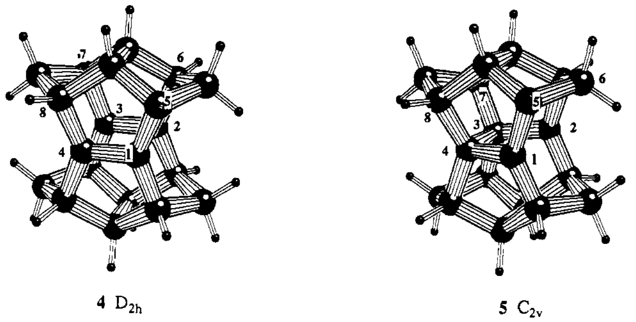
nation of the latter has D_{2h} symmetry **10**.

With optimization at the split valence (3-21G), polarized (6-31G*), and correlated (MP2/6-31G*) ab initio levels, the open form **8** with C_i symmetry is the only minimum (Table I). Both terminal CH_2 groups are twisted 12.5° relative to the plane formed by the carbon atoms. However, at the 6-31G*//6-31G* level the C_i-structure is only 0.1 kcal/mol lower in energy than the planar trans C_{2h} structure. Structures **11** (D_{2h}, σ-aromatic dication) and **12** (C_{2v}, classical dication) are interesting as models for the pagodane and norbornadiene dications. At the SCF level, **12** is more stable than its "σ-aromatic" counterpart **11**, but both have three imaginary frequencies.[15] One of these, mode b of **11** (Figure 4), corresponds to the ring-opening motion toward **12**. At the MP2-correlated level, this frequency mode disappears and **11** becomes more stable than **12**. Optimizing the classical structure **12** at MP2/6-31G* within the C_{2v} point group leads to ring closure to **11**. The two imaginary frequencies a and c remain in **11** at the MP2 level. Frequency mode a describes a distortion toward the rhombic structure **9**, while the out of plane motion c corresponds to a distortion toward the D_{2d} structure **10**. However, the latter has three imaginary frequencies and both **9** and **11** have two. Hence, besides **8**, none of the other forms investigated are even true transition states.

Figure 3, which presents the relative energies at the various theoretical levels, shows that electron correlation is of critical importance for a proper description of structure **9** as well. Improvement of the basis set does not have a large effect on the relative energies of **9**, **10**, and **11**, but upon including the MP2 single-point energy, **9** becomes 38.6 kcal/mol more stable relative to the global minimum **8** and thus more stable than **11** and **10**. At the MP2-optimized level, a second imaginary frequency appears. Thus, **9** is not the transition state of a dyotropic rearrangement as suggested previously, but a stationary point of higher order. The relative order of energies remains constant at the MP2-optimized level and at higher level of correlation (MP3 and MP4SDTQ).

The implications for the pagodane dication on the basis of these model results are obvious. The instability of the classical structure **12** toward the nonclassical **11** (D_{2h} structure) should be even more pronounced in the case of the pagodane dication, where the system is constrained by a molecular framework of D_{2h} symmetry. This is demonstrated clearly by calculations of the pagodanes **4** and **5** with semiempirical and ab initio methods on the 3-21G//3-21G level (Tables II and III). Only with MNDO a minimum structure within the C_{2v} point group was found, which is 4.03 kcal/mol less stable than the D_{2h} structure. Optimizing **5** with MINDO/3 and AM1 as well as 3-21G leads to ring closure to **4**.[2] No energy minimum was found within the C_{2v} point group using these methods. These theoretical results provide good reasons for excluding the set of rapidly equilibrating classical structures **5**.

Table III. Selected Geometrical Parameters of 4 and 5, Calculated with MINDO/3, MNDO, AM1, and ab Initio 3-21G//3-21G



parameter[a]	**4** MINDO/3	**4** MNDO	**4** AM1	**4** 3-21G// 3-21G	**5** MNDO[b]
1–2	2.768	2.592	2.429	2.165	2.518
3–4	2.768	2.592	2.429	2.165	1.723
2–3	1.479	1.461	1.449	1.421	1.512
1–5	1.524	1.511	1.488	1.513	1.514
3–7	1.524	1.511	1.488	1.513	1.559
1–2–6	83.5	86.5	88.8	93.1	88.4
4–3–7	83.5	86.5	88.8	93.1	100.7
2–3–7	111.1	111.6	111.1	111.4	107.9
3–2–6	111.1	111.6	111.1	111.4	109.6

[a] Bond lengths in angstroms and angles in degrees. [b] No MINDO/3, AM1, and 3-21G//3-21G data are given, since no minimum in C_{2v} could be found with these methods.

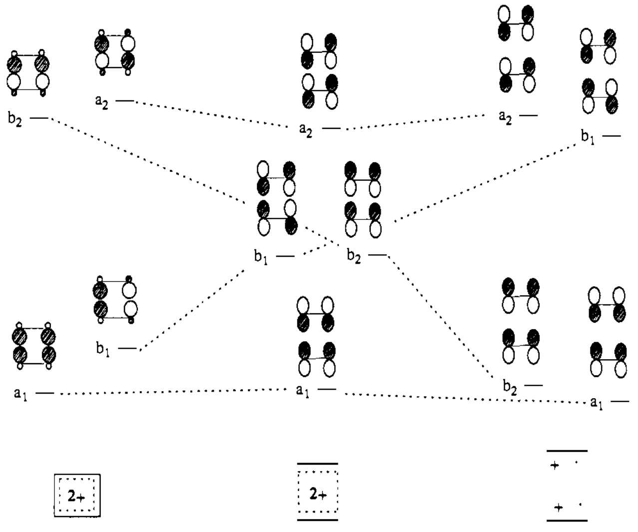


Figure 5. Correlation diagram; cycloaddition of two ethylene radical cations.

However, the singlet diradical cation still remains as a possible alternative to the proposed aromatic species.

Diradical Character of the Pagodane Dication and Related Systems

The pagodane dication **4** can be viewed as a frozen aromatic transition state[16a–c] of the symmetry-allowed cycloaddition of two

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[15] Drewello, T.; Fessner, W.-D.; Kos, A. J.; Lebrilla, C. B.; Prinzbach, H.; Schleyer, P. v. R.; Schwarz, H. *Chem. Ber.* **1988**, *121*, 187.

[16] (a) Evans, M. G. *Trans. Faraday Soc.* **1939**, *35*, 824. (b) Zimmermann, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1564. (c) Dewar, M. J. S. *Tetrahedron Suppl.* **1966**, *8*, 75.

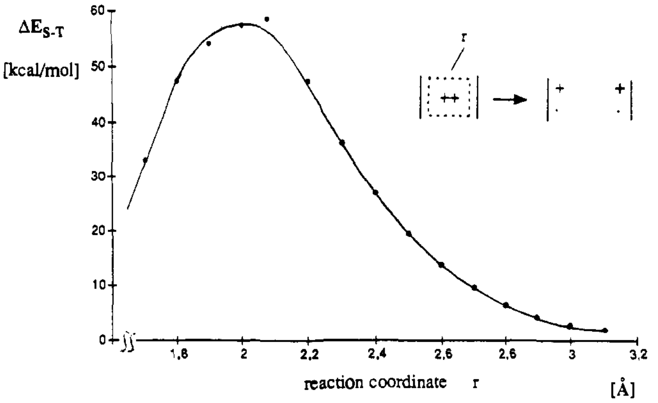

Figure 6. Energy splitting between the lowest singlet and triplet state of the cyclobutane dication system as a function of the reaction coordinate *r*. $\Delta E_{S\text{-}T}$ was calculated with MNDO full CI and imposed D_{2h} symmetry.

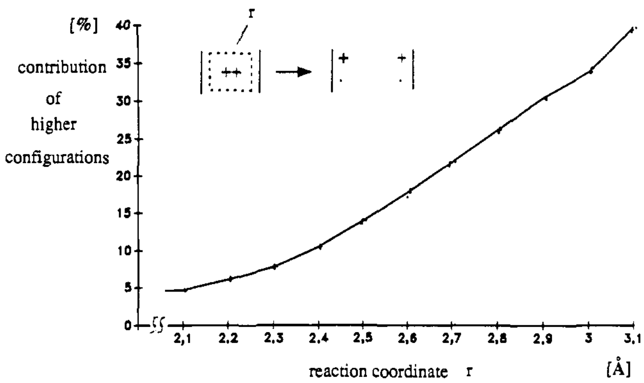

Figure 7. Contribution of higher configurations to the wavefunction of the cyclobutne dication system as a function of the reaction coordinate *r*. The CI eigenvector was calculated with a MNDO full CI calculation and imposed D_{2h} symmetry.

spin-paired ethylene radical cations (Figure 5).

At large distances between the two ethylene radical cation units, the bonding a_1 and the antibonding b_2 MO's are degenerate, and according to Hund's rule, the system should be a perfect diradical. As the distance decreases (within the D_{2h} point group), the energy of the b_2 orbital rises because of its increasing antibonding character and b_1 is stabilized due to the increase in bonding along the reaction coordinate. The b_1 and b_2 levels cross. But since we are dealing with a dication, only the totally symmetric and bonding a_1 orbital is occupied. According to our calculations, this situation is realized in the parent aromatic dication **11**. At this geometry and at all levels of ab initio theory including MNDO, the unoccupied b_1 and b_2 orbitals are almost degenerate. Where does the pagodane dication lie on this reaction coordinate? A bond length of more than 2.5 Å, as predicted by the MNDO calculations, should lead to considerable diradical character. There is a continuum from almost pure closed shell to a diradical nature depending on this geometric parameter. One cannot set a dividing line to clearly distinguish between closed shell and diradical but an indication for a diradicaloid character of a species can be derived from the energy splitting between its lowest singlet and triplet state[17] (Figure 6).

Two ethylene radical cations at an infinite distance involve two degenerate noninteracting and singly occupied MO's. Thus, singlet and triplet states have the same energy and the system is a perfect diradical. Moving to the "transition state" increases the splitting. According to a MNDO full CI calculation, the singlet–triplet splitting in the aromatic dication **11** reaches a maximum value on the reaction coordinate, with 59 kcal/mol indicating a quite pure closed shell state. Shortening the distance even further leads eventually to the square dication, which is again a triplet diradical. Figure 6 shows the singlet–triplet splitting as a function of the bond length *r* between the two formal ethylene radical cation units. Another sign for the "extent" of biradical character can be derived from the contribution of higher configurations to the overall wavefunction. Calculations along the reaction coordinate were performed with MNDO and full CI (Figure 7).

Like the singlet–triplet splitting result, these calculations again predict the geometry corresponding to **11** with $r = 2.2$ Å to have the lowest diradicaloid character along the reaction coordinate. Three configurations account for more than 99.8% of the wavefunction of **11**. This wavefunction ψ can be expressed as a linear combination of the a_1^2 ground state and the two higher configurations b_1^2 and b_2^2 (for definition of the orbitals see Figure 5).

$$\psi = 0.977a_1^2 - 0.141b_1^2 - 0.162b_2^2$$

Thus, the higher configurations account for 4.6% of the wavefunction, indicating a nearly pure closed-shell state. This result has been confirmed by a MC-SCF optimization of **11** with a 3-21G basis set. According to the MNDO CI eigenvector, a proper choice of the valence space should include the a_1, b_1, and b_2 orbitals (HOMO, LUMO, and LUMO+1, Figure 5). A three-configuration MC-SCF optimization using this valence space with a standard 3-21G basis and imposed D_{2h} symmetry predicts the coefficients of the higher configurations b_2^2 and b_1^2 to be 0.2044 and 0.1364, i.e., a contribution of 6% to the wavefunction. For an idealized diradical, like the two ethylene radical cations at an infinite distance, this contribution would be exactly 50% (Figure 7), whereas the "normal" closed-shell 1,4-butadiyl dication **8** shows 1.7% contribution of higher states. Thus, singlet–triplet, MC-SCF, and CI calculations all predict a quite pure closed-shell state for **11**. The diradicaloid character should increase both on shortening and on lengthening the distance between the two formal ethylene radical cation units.

In view of the critical importance of the distance *r* in controlling chemical and physical properties of cyclobutane dication systems (Figures 6 and 7), a reliable estimate for this parameter is needed to determine the electronic structure of the pagodane dication. The results of semiempirical calculations have to be regarded with caution, since these methods have not been parameterized to treat such extraordinary structures. The 3-21G-optimized structure of **11** agrees quite reasonably with the MC-SCF-optimized geometry (*r* is predicted 0.07 Å too short, all other bond lenghts agree within 0.01 Å). Because of technical computer and program limitations, the pagodane dication was optimized with a standard 3-21G basis set. The critical distance *r* in the pagodane was found to be 2.165 Å (Table III), i.e., considerably shorter than the MNDO value (2.592 Å). Even if this distance is ca. 0.07 Å too short, there should be much better overlap between the two formal ethylene radical cation units compared to that expected from the MNDO calculation. According to our CI calculations (Figures 6 and 7), this value lies within the range of lowest diradical character and optimum stability.

Since the electronic structure should strongly depend on this separation parameter *r*, we have examined various conceivable structures (Figure 8).

The dications **13**, **14**, **15**, and **4** have been optimized with a standard 3-21G basis set. With $r = 1.974$ Å, the norbornadiene dication **13** (Figure 8) does have a distance *r* somewhat shorter than the optimum value, but still within the "closed-shell range". A harmonic vibration frequency analysis at the 3-21G level predicts it to be a minimum on the potential energy hypersurface. Indeed, the hexamethyl derivative **7** has been synthesized by Hogeveen et al. via ionization and rearrangement of a tricyclic alcohol.[3]

Structure **14**, whose potential precursor (the corresponding diene) is known,[18] also exhibits a favorable distance *r* (Figure 8).

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(17) For review, see: (a) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92. (b) Bonačić-Koutecky, J.; Koutecky, J.; Michl, J. *Angew. Chem.* **1987**, *99*, 216.

(18) Wiberg, K. B.; Matturro, M. G.; Okarma, P. J.; Jason, E. J.; Dailey, W. P.; Burgmaier, G. J.; Bailey, W. F.; Warner, P. *Tetrahedron* **1986**, *42*, 1895.

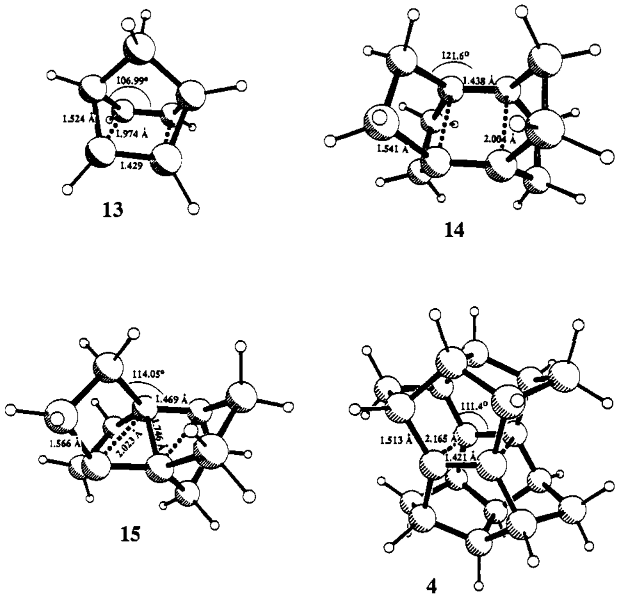
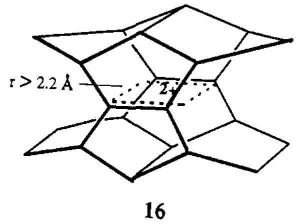


Figure 8. Cyclobutane dication systems with different frameworks and values of the "critical distance" *r*. Geometries were calculated with a standard 3-21G basis set. **13** and **15** were confirmed to be minima by harmonic frequency analysis. **14** is a transition state.

A frequency analysis, however, predicts one imaginary frequency (analogous to mode a in the parent dication). According to further optimization with lower symmetry constraints, **14** turns out to be the transition state of the automerization reaction of a rhomboid structure with C_{2h} symmetry **15** and the two positive charges largely localized at the bridgehead carbons. Experimentally, this tendency is manifested in cross-transannular bonding upon electrophilic attack. Structure **15** was confirmed to be an energy minimum by harmonic frequency analysis. At the 3-21G level, it is 8.6 kcal/mol more stable than D_{2h} **14**. Upon consideration of correlation energy (MP2/3-21G//3-21G), this value is reduced to 1.8 kcal/mol. The cationic system corresponds to the parent rhomboid structure **9** proposed by Hoffmann.[4] Obviously, this system is not as rigid as the norbornane or pagodane framework; it lacks a "cross-bracing" to prevent the system from rhomboid distortion. This "cross-bar" is formed by the CH_2 bridge in **13** and the C–C bond centrally above the four-membered ring in **4**.

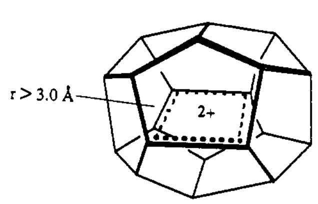
Analogous to [1.1.1.1]pagodane, the [1.1.2.2]pagodane when treated in SO_2ClF solution with SbF_5 at −80 °C is oxidized to give the corresponding dication **16**.[2,19]



16

This cationic species is considerably less stable than the [1.1.1.1] derivative. Even at −20 °C, rearrangement to a bisallylic dication occurs. The instability can be rationalized in terms of larger diradical character. Due to larger bridge sizes (ethylene instead of methylene moieties), the distance *r*, and thus the extent of the diradical character, increases. Side reactions yielding closed-shell cations thus become more probable.

In contrast, the dodecahedrane dication **17** mentioned recently by Prinzbach et al.[20] does not have a chance to profit from aromatic stabilization since the two ethylene radical cation units are separated by a distance of more than 3 Å.



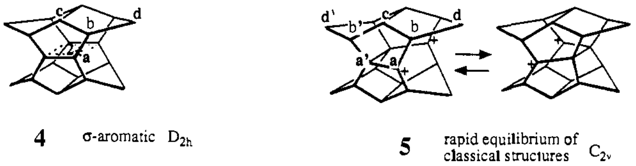
17

Whereas the [1.1.1.1] and [1.1.2.2]pagodane dications are stable in solution, the dications of the corresponding "half-pagodanes" could only be generated in the gas phase by charge-stripping experiments.[15]

^{13}C-Shift Calculations

IGLO ^{13}C-shift calculations[14] have proven to be a powerful tool in structural carbocation chemistry.[21] Comparison of experimental and calculated ^{13}C chemical shift values should provide further evidence in discriminating the structural hypotheses **4–6**. MNDO geometries of the aromatic D_{2h} **4** and the classical **5** as well as the ab initio 3-21G geometry of **4** were used for IGLO calculations performed with DZ basis set (Table IV).

Table IV. Experimental and IGLO Calculated ^{13}C Chemical Shifts of **4** and **5**[a]



	4				5		
	3-21G		MNDO		MNDO		expt[1,2]
	δ[a]	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ
a	241.6	−9.4	261.2	10.2	(417.5 + 101.8)/2 = 259.6	8.6	251.0
b	49.0	−8.2	50.8	−6.4	(64.4 + 46.9)/2 = 55.6	−1.5	57.2
c	47.2	−5.1	49.4	−2.9	(48.4 + 57.5)/2 = 53.0	0.7	52.3
d	53.9	−11.4	64.9	−1.1	45.5	−19.3	65.3

[a] Input geometries are optimized with MNDO and 3-21G. IGLO chemical shifts are calculated with a DZ basis (basis I). [b] Values in parts per million relative to TMS.

Even though there is indication for a σ-aromatic system, the results cannot be interpreted unambiguously in favor of **4**. For both structures, the nonclassical **4** and the classical **5**, rather low-field shifts of the cationic centers a are predicted. The IGLO calculated shift of carbon atoms a in **4** based on the MNDO geometry is 10 ppm low field and the value based on the 3-21G geometry 10 ppm high field compared to the experimental value. Obviously, the predicted chemical shifts are a sensitive function of the geometry.[22] Most surprising are the predicted chemical shifts for the cationic centers in the "open" structure **5**. With δ 259 the average shift (a + a′)/2 is predicted to be within the same range as in the nonclassical compound **4**. The same is true for the nuclei c. In **4**, these carbon atoms are centrally located above the 2π-plane and should be shielded if the ring current were

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[19] Fessner, W.-D.; Sedelmeier, G.; Spurr, P. R.; Rihs, G.; Prinzbach, H. *J. Am. Chem. Soc.* **1987**, *109*, 4626.

[20] Melder, J.-P.; Pinkos, R.; Fritz, H.; Prinzbach, H. *Angew. Chem.* **1989**, *101*, 314.

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[22] Experience has shown that accurate geometries are needed (optimized on a correlated level) to obtain reliable chemical shifts for cations with IGLO (see ref 21). MNDO and 3-21G geometries differ largely.

[23] Sustmann, R.; Daute, P.; Sauer, R.; Sicking, W. *Tetrahedron Lett.* **1988**, *29*, 4699.

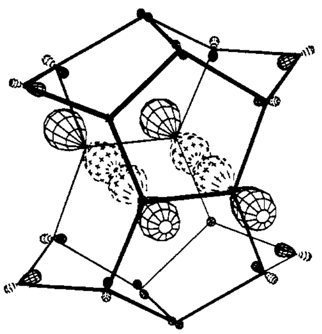

Figure 9. HOMO of the pagodane dication. Coefficients are calculated with MNDO and plotted with PERGRA.[23]

present. The change in chemical shift in going from pagodane (δ 59.6) to **4** (δ 52.3) is in the expected direction, although the change is small. Our IGLO calculations agree, but a similar upfield shift is predicted for the classical structure **5** (calculated δ 53.01, observed δ 52.3). The upfield shift has been interpreted in terms of a ring current in **4**.[2] On the basis of the IGLO results, however, this does *not* exclude a classical structure. Obviously, in the field of dications shielding and deshielding effects have to be interpreted very carefully. They cannot unequivocally be interpreted to be due to a ring current or any aromaticity effect, as this is usually the case with neutral compounds.

In contrast to c, the nuclei d should be located within the deshielding range of the ring current. Fortunately, in this case the interpretation is less ambiguous. IGLO predicts a downfield shift for the aromatic structure **4** ($\Delta\delta$ = 12 ppm, 3/21G, $\Delta\delta$ = 22.4 ppm, MNDO) compared to the neutral pagodane **1** and an almost constant value for the nonclassical ion **5** ($\Delta\delta$ = 3.6 ppm). The experimental value ($\Delta\delta$ = 23.4 ppm) clearly favors a nonclassical structure.

Aromaticity of Cyclobutane Dicationic Systems

There is an inherent difficulty in answering the question whether a given compound is aromatic or not. In contrast to energy and geometry, aromaticity is not a quantum theoretical observable (operator acting on a wavefunction leading to an expectation value) and thus not a yes or no question. Usually, the term aromatic is justified by the examination of observables like bond alternation (geometry), stabilization versus any reference (energy), nuclear magnetic resonance, etc. Since the electronic structure (aromaticity) of the pagodane dication is a consequence of its D_{2h} symmetry, we first determined the structure. According to our calculations, there is little doubt that the pagodane dication has D_{2h} symmetry since we disproved the two alternatives (C_{2v} equilibrium **5** and diradical structure **6**), which also comply with the experimental data.

After having elucidated the geometry, we turn to the question of if the electronic structure of the pagodane dication should be termed aromatic. We have reasons for an affirmative answer.

The two-electron delocalized system in the pagodane dication is built up by a set of four MO's, which are equivalent to those of the model compound the rectangular cyclobutane dication **11** (Figure 1). As shown in Figure 9 for the HOMO of pagodane dication, the coefficients at other carbon atoms in the pagodane framework are low (<0.1).

Thus, there is no significant conjugative effect of orbitals of the pagodane framework disturbing the topology of the four cyclobutane orbitals. The four MO's describing the four-center two-electron delocalized system are separable from those describing the molecular frame in a first-order approximation. The pagodane framework merely holds the delocalized system together and can thus be compared with the σ-frame in benzene and related aromatic systems.[24]

Since the sets of MO's for both the cyclobutane and cyclobutadiene dication are topologically equivalent, all arguments for aromaticity in the cyclobutadiene dication should also be qualitatively valid for cyclobutane dication and hence for pagodane dication and related systems. This analogy is still valid on a quantitative level. The interaction of the p orbitals building up the delocalized system can be rationalized by analyzing their contribution to the overall bond orders. There are two different modes of overlap involved in the cyclobutane dication system. One is of π-character along the shorter side of the rectangle and the other is σ on the longer side. According to a natural bond order analysis,[25] both interactions are almost equivalent even though the bond lengths differ strongly (Figure 10).

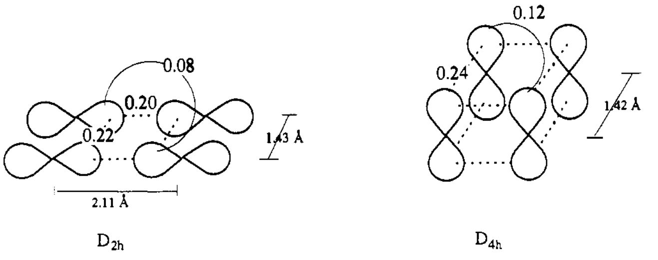

Figure 10. Natural bond orders in the HOMO's of rectangular cyclobutane dication (D_{2h}) and square cyclobutadiene dication (D_{4h}), calculated with 6-31G*//6-31G*.

Orbital overlap of two carbon p orbitals separated by a distance of 1.43 Å in a π-bond is of the same order (0.23) as a σ-overlap with a bond distance of 2.11 Å (0.21).[26] Both bond orders compare well with the π-bond orders in the square cyclobutadiene dication, and both orbitals are of similar energy (−0.9 eV in cyclobutane and −0.89 eV in cyclobutadiene dication). Thus, any stabilization arising from delocalization of the two electrons should be roughly of the same magnitude in both systems.

Following the original definition of σ- and π-bonds, which defines orbitals lying in the plane of a planar π-system as σ and those perpendicular to the plane as π, the pagodane dication and related systems contain perfectly σ-delocalized systems with two electrons. A similar σ-delocalization was discussed by Dewar[27-29] and Cremer[30,31] for cyclopropane. Most of the unusual properties of cyclopropane are convincingly explained assuming a σ-aromaticity, even though Cremer[31] criticized the term σ-aromaticity since "it applies essentially to one class of compounds, namely the cyclopropanes." Rectangular cyclobutane dications could now be viewed as a second class.

Delocalization in rectangular cyclobutane dication systems, however, can be clearly distinguished from the concept of σ-conjugation introduced by Dewar and Petit,[32] which is based on the fact that resonance integrals between different hybrid AOs of a given atom do not vanish even if the AOs are orthogonal. In rectangular cyclobutane dication **11** as well as in the pagodane dications **4** and **16**, the AOs involved in the delocalized system are almost pure p orbitals (Figure 9).

Separability of the delocalized system (Figure 9), cyclic delocalization (Figure 10), $4n + 2$ electrons, together with ^1H and ^{13}C NMR data,[2] and cyclovoltammetry of **4**[33] justify the term aromatic. Even though a stabilization cannot be expressed quantitatively because the choice of the reference compound is arbitrary, stabilization should be of the same order as in the cyclobutadiene dication.

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(29) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669.

(30) (a) Cremer, D.; Binkeley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1974**, *96*, 6900. (b) For examples of "in-plane-aromaticity" see: McEwen, A.; Schleyer, P. v. R. *J. Org. Chem.* **1986**, *51*, 4357.

(31) Cremer, D. *Tetrahedron* **1988**, *44*, 7427.

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Conclusion

For a rectangular, σ-aromatic cyclobutane dication, like the pagodane or the norbornadiene dication, to be stable, some prerequisites are essential:

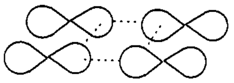
(1) A rigid molecular framework is needed to prevent in-plane distortion toward the rhomboid form or out of plane motion toward D_{2d} symmetry (imaginary vibrational frequency modes of the parent compound **11**, Figure 4).

(2) The two formal ethylene radical cation units have to be held at distances between ~1.9 and 2.3 Å to keep the diradicaloid character low enough to prevent side reactions.

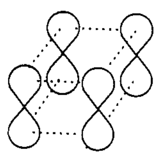
Another conclusion can be drawn from the numerous experiments aimed at oxidizing cyclobutane containing compounds: the cyclobutane system has to be octasubstituted, perhaps due to both kinetic and thermodynamic stabilization.[34]

The pagodane dication and the norbornadienyl dication can be viewed as frozen aromatic transition states of the reaction of two ethylene radical cations in the sense of the Dewar/Evans principle.[16] A cycloaddition of two neutral ethylene molecules in D_{2h} symmetry is forbidden because the transition state would be antiaromatic (triplet diradical), while the product cyclobutane again is closed shell. Removing two electrons from the system reverses the picture. The educts are two ethylene radical cations, the transition state is aromatic (almost pure closed shell), and the product, the square cyclobutane dication, again is diradical. The formal transition state now is a minimum on the reaction path within D_{2h} symmetry because of its aromatic stabilization. This stabilization, however, has to be paid for by a strong Coulomb repulsion of the two positive charges. If the system is not constrained within a D_{2h} symmetry by a rigid molecular framework, the charges will be separated by distortion toward a rhomboid or tetrahedral geometry and bishomoaromaticity will be canceled. Hence, it should be possible to synthesize molecules corresponding to some other points on the reaction coordinate and thus test the limits of homoaromaticity.

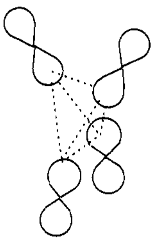
The rectangular cyclobutane dication is also interesting from another point of view. It is the third in a set of topologically different two-electron four-center hydrocarbon aromatic compounds, which have been verified experimentally.



D_{2h}



D_{4h}



T_d

None of these ideal arrangements is an energy minimum without extra stabilization by substitution. The square D_{4h} cyclobutadiene dication is a transition state for the ring inversion of the puckered structure.[21a,35] The tetrahedral dication needs six CH_2 bridges on all edges of the tetrahedron (realized in the adamantane framework)[21b] to be a relative minimum on the energy hypersurface. Their instability notwithstanding, such dications can serve as models illustrating the concepts of aromaticity and isolobal structures.

Acknowledgment. We thank the Fonds der Chemischen Industrie for support through a Liebig Stipendium to R.H. GAUSSIAN82 calculations were carried out on a CONVEX C1; we thank the CONVEX Computer Corp. for support, the Leibniz Rechenzentrum in Munich for providing supercomputing time on a CRAY X-MP/24 and a Cray Y-MP4/432, and Dr. A. J. Kos for early calculations on $C_4H_8^{2+}$.

Registry No. 4, 99828-64-5; **15**, 132646-10-7; ethylene radical cation, 34470-02-5; 1,4-butanediylium, 111160-98-6; norbornadiene dication, 132832-60-1.

Supplementary Material Available: Full calculational details of ab initio calculations of **4**, **13**, **14**, and **15** (20 pages). Ordering information is given on any current masthead page.

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[34] Norbornadiene or quadricyclane cannot be oxidized to form the corresponding dication. Reaction with SbF_5 in SO_2ClF even at very low temperatures occurs violently to form black polymers. Herges, R.; Prakash, G. K. Unpublished results. For other unsuccessful attempts to oxidize cubane, homocubane, bishomocubane, and related, not fully substituted cyclobutane systems, see: ref 2, p 7767.

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Structures of Ag_2X^+ and Cu_2X^+ Ions: Comparison of Theoretical Predictions with Experimental Results from Mass Spectrometry/Mass Spectrometry

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Abstract: Daughter ion MS/MS mass spectra have been recorded for Ag_2X^+ and Cu_2X^+ parent ions in which X is H, CH_3, O, or CO. Consideration of the dissociation processes observed suggests the prevalence of certain ion structures out of the several possible for these combinations of atoms. The suggested structures are compared with theoretical predictions based on Hartree-Fock SCF calculations using the relativistic ECP approximation. Present theoretical results agree with the rationalizations of the daughter ion MS/MS experiment in the assignment of a linear structure to Ag_2H^+, Ag_2O^+, and Cu_2O^+. Theoretical predictions of linear $Ag_2CH_3^+$ and $Cu_2CH_3^+$ are also supported by experimental work with mass spectrometry/mass spectrometry. Bent geometries are predicted for Ag_2CO^+ and Cu_2CO^+ by the calculations performed.

Introduction

Mass spectrometry/mass spectrometry (MS/MS) is a powerful tool for ion structure elucidation.[1] To record a daughter ion MS/MS spectrum, a parent ion of specified mass is selected from all ions formed in the source of the mass spectrometer, excited

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[1] Busch, K. L.; Glish, G. L.; McLuckey, S. A. *Mass Spectrometry/Mass Spectrometry: Techniques and Application of Tandem Mass Spectrometry*, VCH Publishers: New York, 1988.

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