The $C_6R_6^{2+}$ (Benzene Dication) System[1]

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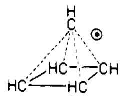
Abstract: MINDO/3 Calculations are reported for the benzene dication (**2a**), for its hexachloro (**2c**), hexamethyl (**2d**), and hexafluoro (**2e**) derivatives, and for the hexaoxy anion (**2b**). Two stable isomers were found for **2a**, **2c**, **2d**, and **2e**, one corresponding to a symmetrical pentagonal pyramid and the other to a structure similar to that of the chair conformer of cyclohexane. Both isomers of **2a**, and both of **2d**, have similar energies, each pair being separated by quite a high barrier, while the chair forms of **2c** and **2e** are the most stable. Planar forms of all five isomers also corresponded to minima on the potential surfaces. Four minima were found for **2b**: one a distorted pyramid, one a chair, one planar, and the last a boat, the boat being the most stable. **2a**, **2b**, and **2d** are predicted to have singlet ground states while the triplet chair form of **2c** and the triplet planar form of **2e** seem to be the most stable. These results agree with experiment and lead to various predictions. MNDO calculations for **2a** were less satisfactory.

The majority of "nonclassical" carbocations may be represented[2] as π complexes derived from an olefin as the donor and a classical carbocation as the acceptor, a formulation first suggested by Dewar[3,4] some time ago. There is, however, no reason why more complicated π systems should not serve as donors in analogous π complexes. Indeed, the π complex theory was originally introduced[3] to explain the course of the benzidine rearrangement, the intermediate in this being formulated as a π complex in which phenylamino and phenylimino units act as the donor and acceptor. In recent years analogous carbocations have been the subject of extensive study,[5] the first to be recognized[6] being the pyramidal isomer (**1**) of $C_5H_5^+$. Here we will be concerned with another possible example, the dication $C_6R_6^{2+}$ (**2a**). Such "nonclassical" structures have long been recognized in the boron hydrides and carboranes, **1**, for example, being an analogue of pentaborane (**4**) and **3a** an analogue of a dicarbotetraborane (**5**).



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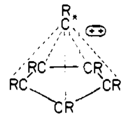
$(CR)_6^{++}$

2 a, R=H
b, R=OH
c, R=Cl
d, R=CH_3
e, R=F



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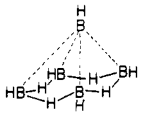

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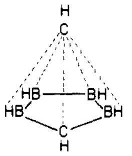
Ab initio calculations[7] predicted a pyramidal structure (**3a**) to be a minimum on the potential surface for the parent ion, a conclusion also supported by MINDO/3[7c] and MNDO.[7c] These findings confirmed previous NMR evidence[8] for a pyramidal geometry (**3d**) in the case of the hexamethyl derivative. MINDO/3, however, also predicts[7c,9] the existence of a second stable isomer with a chair geometry, best represented (see **6a**) as containing a pair of allyl cation units linked by C–C single bonds.



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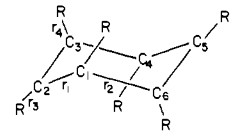

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Other investigations, both theoretical and experimental, have also led to conflicting conclusions concerning the ground-state structures of derivatives (**2a–e**) of the parent ion (**2a**). The first of these ions to be studied,[10] a salt ($K_4C_6O_6$) whose anion can be regarded as a hexaoxy derivative (**2b**) of **2a**, was claimed to exist as a ground-state singlet with a chair geometry. But ESR studies[11] of the hexachloro derivative (**2c**) have shown it to have a triplet ground state, probably with D_{6h} symmetry.

Since no systematic attempt has been made to establish the relationship between the alternative structures or the effect of substituents on their relative energies, we decided to carry out calculations for a number of derivatives of these ions in the hope of obtaining such information.

MINDO/3[12] has previously been shown to give results for simple carbocations which are similar[13] to those from high-level ab initio calculations[14] employing large basis sets and allowing specifically for electron correlation by very extensive CI or some comparable procedure. MINDO/3 calculations for a number of other systems involving carbocations, including **1**, have moreover given very satisfactory results.[15] While there is no guarantee that

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[1] Part 67 of the series "Ground States of Molecules". For Part 66, see: Dewar, M. J. S.; Reynolds, Charles H. *J. Am. Chem. Soc.* **1984**, *106*, 1744.

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[15] In particular MINDO/3 gives very reasonable results for **1**; see: Dewar, M. J. S.; Haddon, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 5836; **1974**, *96*, 255.

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Table I. MINDO/3 and UMINDO/3 Heats of Formation (kcal/mol) of Singlet and Triplet Dications and Parent Hydrocarbons

compd	RHF singlet	UHF triplet
3a	551.9[a,b]	596
6a	552.5[b]	555
7a	563.8	562.8
22a	547.2	583
8a	28.4	
3b	320	308
6b	278	272
7b	282	274
20	274	273
3c	534	550
6c	510.5	507
7c	515	509
8c	-0.03	
3d	473.9[a]	496
6d	473.3	472
7d	492	488
22b	496.0	
8d	21.8	
3e	374	379
6e	330	324
7e	329	323
8e	-230.5	

[a] Unpublished calculations in these laboratories by Dr. Donna J. Nelson, which we have repeated. [b] Lammertsma and Schleyer[7c] reported MINDO/3 values of 552.5 and 551.9 kcal/mol for **3a** and **6a**, respectively.

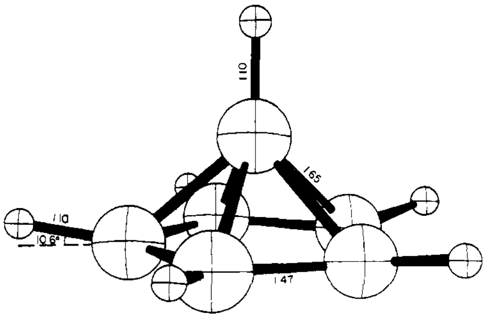


Figure 1. Geometry calculated for pyramidal $C_6H_6^{2+}$ (**3a**).

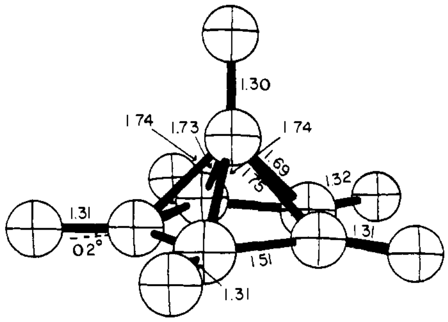


Figure 2. Geometry calculated for the pyramidal form (**3b**) of the hexaoxy ion.

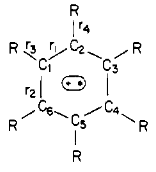
it will be equally successful for dications and while there are indeed reasons[16] for believing that it may tend to systematically overestimate their stabilities, it was clearly the method of choice for our purpose. We have therefore used it to study the essential parts of the potential surfaces for $(CH)_6^{2+}$ and several of its derivatives. Preliminary MINDO/3 calculations here, by Dr. Donna J. Nelson, had confirmed the earlier conclusion[7] that the pyramidal form (**3a**) of **2a** is stable and had shown that similar conclusions hold for **3d**. Here we report extensive surveys of the corresponding singlet and triplet potential surfaces, together with analogous calculations for three other derivatives of **2a**.

Procedure

The calculations were carried out by using our standard MINDO/3 program,[12] available from QCPE as part of the MOPAC package.[17] Geometries were fully optimized with no assumptions, using the Davidon–Fletcher–Powell method. Transition states were located by the reaction coordinate method and refined by minimizing the norm of the gradient.[18] All stationary points were characterized by calculating force constants.[18] The energies of triplet states were found by the spin-unrestricted version (UMINDO/3) of MINDO/3. For comparison, some of the calculations were repeated using MNDO.[19]

Results and Discussion

Calculations were carried out for the parent ion (**2a**), for the tetraanion (**2b**) derived by loss of six protons from its hexahydroxy derivative, and for the hexachloro (**2c**), hexamethyl (**2d**), and hexafluoro (**2e**) derivatives of **2a**. Both singlet and triplet versions of each isomer were examined. Three possible geometries were considered in each case, i.e., the pyramidal structure (**3**), a nonplanar monocyclic structure (**6**), and the planar structure (**7**). All corresponded to minima on the relevant potential surfaces. The geometries of the planar ions (**7**) were calculated with enforced planarity, assuming that they would prove to be the transition states for interconversion of mirror image chair isomers. Force constant calculations,[18] however, showed that they were minima on the potential surface. Calculations were also carried out for the interconversions of **3a** and **6a** and of **3d** and **6d**.



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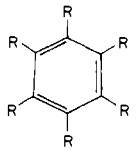
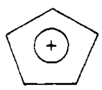


8 a R=H
c R=Cl
d R=CH_3
e R=F



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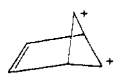

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A. Pyramidal Ions. Each ion was found to occur in a pyramidal form, **3**, as previously reported[7] for **3a** and for its hexamethyl derivative (**3d**).[8] The MINDO/3 heats of formation of the corresponding singlets and triplets are given in Table I; those for the analogous neutral benzene derivatives (**8**) are also listed for comparison.

All of these species were predicted to have singlet ground states and all except **3b** had C_{5v} symmetry, although no symmetry was imposed in the calculation. The basal groups in each ion were tilted upwards, out of the plane of the five-membered ring toward the apex of the pyramid (see Figure 1). The parent system (**3a**) had a basal group tilt of 10.6°, in agreement with the STO-3G (3-21G) value of 11.7° (8.2°).[7b] In the case of **3b**, a minimum corresponding to a distorted pyramid (Figure 2) was found on the potential surface.

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(16) The core-electron attractions are estimated in MINDO/3 by using the Goeppert-Mayer potential with neglect of penetration integrals and are consequently too small. This is compensated by an empirical reduction in the core–core repulsions. However, since the same correction is also applied in the case of dications, the repulsions between the positive charges in the latter are likely to be underestimated. Similar considerations apply to MNDO.

(17) MOPAC is a complete package of programs for calculations using MINDO/3 or MNDO. It includes options for CI, for calculations using the UHF or "half-electron" approximations, for the calculation of force constants, vibration frequencies, and derived thermodynamic properties (entropies, specific heats), and for the location of transition states, by the reaction coordinate method, by minimizing the norm of the gradient,[25] or by a new procedure we have developed. Geometries are found by a gradient optimization procedure, based on the Davidon–Fletcher–Powell algorithm. Stationary points are characterized by calculating and diagonalizing the Hessian (force constant) matrix.[18] Versions are available (from QCPE) for Digital VAX series, IBM, and CDC computers.

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Table II. MINDO/3 (3-21G)[7b] Optimized Geometries (Distances in Å, Angles in deg)[a] of Singlet Pyramidal Species, **3a–e**

compd	a^b	C_B–C_B	C_B–R	C_A–R	C_A–C_B	θ
3a	1.20 (1.234)	1.47 (1.442)	1.10 (1.073)	1.10	1.65 (1.740)	10.6 (8.2)
3b	*c*	1.51	1.31	1.30	1.73	0.2
3c	1.22	1.49	1.72	1.73	1.67	7.2
3d	1.25	1.50	1.50	1.50	1.70	3.4
3e	1.22	1.48	1.35	1.36	1.66	11.0

[a] B = basal carbon atom; A = apical carbon atom; θ = amount of upward bending by the substituent (in deg). [b] Distance from the center of the ring to the apical carbon atom. [c] Since this species is unsymmetrical, the value for *a* has been omitted. The apical–basal distance listed is an average value.

Table III. MINDO/3 Charges for Singlet Pyramidal Species, **3a–e**

compd	C_A	C_B	R_A	R_B
3a	0.18	0.14	0.19	0.18
3b	0.34	0.21	−0.89	−0.90
3c	0.18	0.18	0.16	0.15
3d	0.18	0.11	0.21	0.22
3e	0.26	0.36	0.01	−0.01

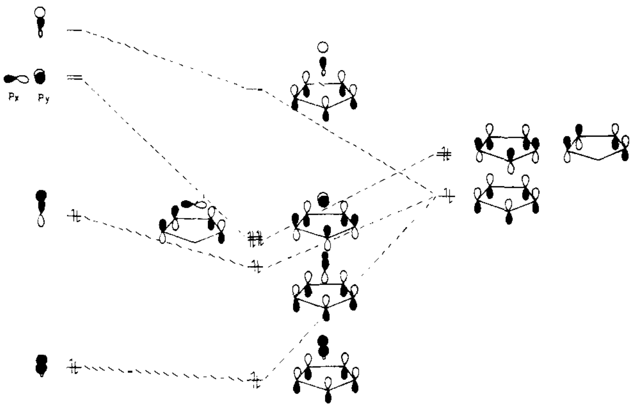

Figure 3. Orbital correlation diagram for **3a**.

The heats of formation of the pyramidal ions (**3**) from the corresponding benzene derivatives (**8**), i.e., the double-ionization energies, can be estimated from the data in Table I; i.e.

3a, 524.1; **3c**, 534.0; **3d**, 472.9; **3e**, 604.5 kcal/mol (1)

As would be expected, introduction of methyl substituents into **2a** lowers the double-ionization energy while chlorine and fluorine increase it.

Table II shows the bond lengths calculated for the various ions and Table III the corresponding formal charge at each atom in them. The reported[7b] ab initio values for **3a** are included for comparison.

The stabilization of **3d** by the methyl groups is accompanied by an increase in the skeletal C–C bond lengths, by 0.03 Å (C–C) and 0.05 Å (C–C*), and by a dispersal of charge onto the basal methyl substituents (charge on each basal hydrogen atom in **3a**, +0.18, and on each basal methyl group in **3d**, +0.22). The net charge on the carbon skeleton is therefore less in **3d** than in **3a**, as would of course be expected, whatever the mode of electron release by methyl. The charge on the apical carbon remains, however, the same in both cases, +0.18.

Although the ^{13}C chemical shift of 22.5 ppm[8a] has been interpreted as indicating low positive charge at the apical carbon, in agreement with the early STO-3G calculation,[7a] the chemical shift of a carbon atom depends greatly on the types of bonds it forms, as well as its net formal charge. Since there are no analogies for **3a**, there is no way to predict what the chemical shift of the apical carbon would be if it were neutral.

Moreover, simple qualitative arguments account well for the MINDO/3 calculated positive charge at the apical carbon. If **3a** is regarded as a π complex formed by combination of $C_5H_5^+$ (**9**) with CH^+, as indicated in Figure 3,[20] the interaction between the filled π MO of **9** and the empty hybrid AO of CH^+ gives rise to a σ-type dative bond, while the interactions between the two singly occupied π MOs of **9** and the two singly occupied p AOs of CH^+ give rise to two equivalent π-type bonds. The inductive transfer of negative charge from the methyl groups to the adjacent carbon atoms should make the latter uniformly less electronegative. This change will reduce the resonance integrals between the skeletal carbon atoms.[21] The triple μ bond in **3** should therefore become weaker and correspondingly longer. Since dative bonds become more polar the longer they are and the smaller the resonance integrals between the atoms forming them,[22] the methyl groups in **3d** should then make it more polar, leading to a drift of electrons from the apical carbon atom to the basal atoms. The resulting increase in positive charge on the apical carbon atom will compensate the opposing effect of the methyl substituent.

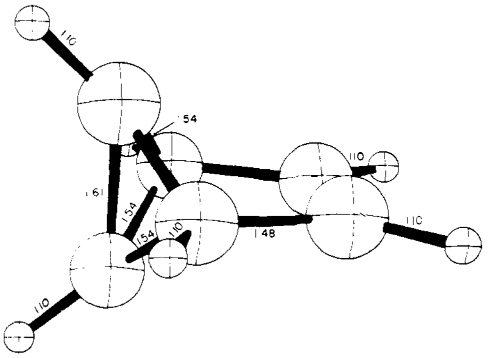

Figure 4. Geometry calculated for triplet **10a**.

Since chlorine and fluorine are +*I* substituents,[23] the same arguments suggest that their introduction into **3a** should lead to a general decrease in the CC bond lengths. However, both chlorine and fluorine have unshared p electrons and therefore also act as −*E* substituents.[23] The resulting conjugative interactions in **9** should reduce the strengths of the CC π bonds, countering the decrease due to the +*I* effect of halogen. The calculated bond lengths indicate a small net increase in each case. The electron-releasing effect of O must be especially great because of its negative charge. The CC bond lengths in **3b** are correspondingly long. Indeed, the decrease in the strength of the μ bond linking the C_5 and C moieties in **3b** leads to disruption of the pyramid (Figure 2).

Because **3a** has a closed-shell structure where all the bonding MOs are filled and all the antibonding ones empty, any additional electron would have to occupy an antibonding MO. This is one reason why the nonclassical structure is so stable. In spite of its double positive charge, it has little tendency to undergo reduction or to act as an electrophile. The situation in ions of this kind has been formulated in terms of an "eight-electron rule" by Minkin and Minyaev[24] and as a "(4*n* + 2) interstitial electron rule" by Jemmis and Schleyer.[7b] The closed-shell structure of **3a** also implies that triplet **3** must be much higher in energy than the singlet, being indeed a typical triplet excited state. As Table I shows, this is true for all the pyramidal ions, other than **3b**, where

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(20) See ref 7b, 8a, and 24 for similar correlation diagrams.

(21) This follows from the Mulliken (Wolfsberg–Helmholtz) approximation. See: Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969; pp 80, 87.

(22) See ref 21, p 120.

(23) See ref 21, section 9.13.

the effects of the substituents are sufficient even to destroy its symmetry.

Since **3** should have a degenerate HOMO if it has C_{5v} symmetry, it follows that the triplet form of **3** should undergo Jahn–Teller distortion from fivefold symmetry. This is indeed the case. The triplet ions all adopted a bicyclic structure, corresponding to the bicyclo[2.1.1]hexen-5,6-diyl dication (**10**). Figure 4 shows the structure calculated for the parent ion, **10a**.

There is no reason in principle why **10** should not also represent a stable isomeric form of the singlet ion. However, no minimum corresponding to such a species could be found on any of the singlet potential surfaces. The nearest to it is the structure found for **3b** which could perhaps be regarded as a cross between it and the symmetrical pyramid.

B. Monocyclic Chair Isomers. Since benzene also has a degenerate HOMO, the corresponding singlet monocyclic dication should, like the radical (mono)cation, undergo Jahn–Teller distortion. Indeed, as previously noted, a second structure for **2a** not only has bonds in the ring which are unequal in length but the ring itself is also distorted from planarity. Such distortions would be expected if planar **2a** is antiaromatic, analogous to the structure calculated[15] by MINDO/3 for monocyclic $C_5H_5^+$. The changes in bond length and distortion from planarity would serve to isolate the two allylic systems in **2a**, thus minimizing the unfavorable cyclic conjugation. The distortion may also serve to reduce the Coulombic repulsions in the dication; however, this factor alone would not account for its nonplanarity.

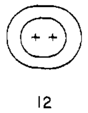
Before discussing whether or not **2a** is indeed antiaromatic, we must first determine what the term "aromatic" means, since it has been used recently in a variety of connotations. The term was first introduced by organic chemists to describe cyclic compounds which, while formally unsaturated, failed to undergo reactions characteristic of acyclic analogues. The development of quantum theory and thermochemistry showed that the special behavior of aromatic compounds was due to unusual stability, arising from a cyclic delocalization of electrons that also leads to bond lengths intermediate between those of single and double bonds.

Hückel originally concluded[25] that a symmetrical cyclic polymethine has a closed-shell structure only if it contains $(4k + 2)$ π electrons. Rings with $4k$ π electrons have pairs of electrons occupying pairs of degenerate HOMOs and should therefore have triplet ground states. This argument, however, applies only to monocyclic hydrocarbons and even then only if the ring has D_{nh} symmetry. It provides no justification for extension of the rule to polycyclic systems or to systems containing heteroatoms, and it also fails to give any indication that the $4k$-membered rings should be less stable than those with $(4k + 2)$ members.

The first general treatment of aromaticity in terms of the stability of the molecules in question was given 30 years ago using PMO theory.[26a] It showed that $4k$-electron rings are not merely not aromatic but are antiaromatic,[28] i.e., destabilized relative to open-chain analogues. Although the original treatment applied only to monocyclic and bicyclic systems, it was later used[27] to derive a more general form of Hückel's rule that can be applied to polycyclic systems. This approach remains the only general, valid treatment of aromaticity in the original sense of the term. In recent years the situation has been complicated by the use of other criteria of aromaticity, in particular magnetic effects displayed in NMR spectra. These, however, have no direct bearing on the chemical peculiarities that represent the real criterion of aromaticity, so their use as a definition of aromaticity is both incorrect and confusing. The energy criterion is valid because, and only because, the chemical peculiarities in question are due solely to the energetics of the molecules involved.

The aromaticity or antiaromaticity of a neutral conjugated system depends on its energy relative to that of an analogous species with a similar cyclic structure but without cyclic conjugation. The latter is of course purely hypothetical so its energy has to be estimated in some way from data for acyclic analogues. In the case of a neutral hydrocarbon, this presents no problems, because the reference species has localized bonds and its energy can therefore be estimated by using appropriate bond energies. The situation in an ion, or diion, is more complicated because the bonds in an analogous acyclic species are also delocalized, cf. cyclopropenyl with allyl. Attempts to estimate the energies of the (cyclic) reference ions from data for open-chain analogues are complicated by the additional Coulombic repulsions in the former, particularly in diions. It is therefore much harder to quantify aromaticity and antiaromaticity in ions than it is in neutral molecules. This problem becomes acute in the case of diions where the additional Coulombic repulsions are very large. No conclusions concerning their aromaticity can be drawn from comparisons with acyclic analogues. For example, the fact that cyclobutadiene diions have not been prepared is no indication that they are not aromatic, because the repulsion between the charges in an analogous nonaromatic ion are so large. The aromatic species would still be very unstable even if its aromatic energy was very large.

Returning now to **2a**, while one might assume planar **2a** to be antiaromatic because it contains four π electrons, the use of Hückel's rule in this connection is unjustified because current derivations of the rule, including the PMO one, apply *only* to species where the number of π electrons is equal to the number (N) of conjugated atoms, or, in cases where N is odd, to $(N \pm 1)$. The original PMO treatment,[26a] where only first-order perturbations were considered, is indeed limited to these cases. It can, however, be extended in the following way to dications and dianions (N even) by an analogous use of second-order perturbation theory.



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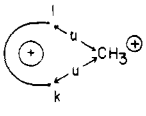

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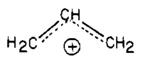

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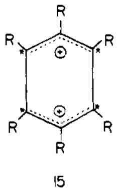

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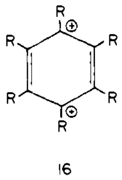

16

Consider first a dication, $(CH)_n^{2+}$. Both the open-chain ion (**11**) and its cyclic analogue (**12**) can be derived by union[26b] of an odd AH cation, $(CH)_{2n-1}^+$ (**13**), with a methyl cation, CH_3^+, see **13**. From symmetry, the coefficients $(a_{\mu 1}, a_{\mu k})$ of the AOs (ϕ_1, ϕ_k) of the terminal atoms $(1, k; k = 2n - 1)$ in the MO Ψ_μ of **13** obey the relation:

$$a_{\mu 1} = \pm a_{\mu k} \qquad (2)$$

The sign is positive if Ψ_μ is symmetric and negative if it is antisymmetric, for reflection in the plane of symmetry indicated in

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[24] Minkin, V. I.; Minyaev, R. M. *Zh. Org. Khim* **1979**, *15*, 1569; *J. Org. Chem. USSR* (*Engl. Transl.*) **1979**, *15*, 1401.

[25] Hückel, E. *Z. Phys.* **1931**, *70*, 204; **1932**, *76*, 628.

[26] (a) Dewar, M. J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3341, 3345, 3350, 3353, 3355, 3357. (b) Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum Press: New York, 1975.

[27] Dewar, M. J. S. *Tetrahedron Suppl.* **1966**, *8*, 75.

[28] Although the destabilization of $4k$-electron systems was not specifically pointed out in the original papers because of the (then current) hostility to speculation and the lack of any examples, this obvious conclusion and the equally obvious term "antiaromaticity" were presented in lectures from 1952 onward. The term was introduced independently, and simultaneously, into the literature by Dewar[27] and Breslow: Breslow, R. *Chem. Eng. News* **1965**, *43*, 90.

Table IV. MINDO/3 Optimized Geometries (Distances in Å, Angles in deg) of Singlet and Triplet Chair Species, **6a**–e, and Singlet Boat Species, **20**

species		r_1	r_2	r_3	r_4	$C_1C_2C_3$	$C_2C_3C_4$
6a	singlet	1.40	1.46	1.11	1.10	108.5	124.6
	triplet	1.43	1.43	1.11	1.11	119.1	119.8
6b	singlet	1.52	1.41	1.32	1.26	123	117
	triplet	1.51	1.48	1.29	1.30	120.2	117.4
6c	singlet	1.41	1.48	1.71	1.73	111.8	121.2
	triplet[a]	1.44	1.44	1.71	1.71	114.7	122.3
6d	singlet	1.44	1.50	1.49	1.50	109.1	121.6
	triplet	1.46	1.46	1.49	1.49	117.9	117.5
6e	singlet	1.38	1.50	1.31	1.36	115.0	123.0
	triplet[a]	1.44	1.45	1.33	1.33	115	122
20	singlet	1.53	1.41	1.325	1.255	120.3	114.1

[a] The calculated geometry showed small irregular variations from the C_{2H} symmetry exhibited by the other isomers. The values listed are averages for bonds and angles that would be equal under C_{2h} symmetry.

Figure 5a. The MOs of **13** alternate in symmetry with increasing energy, the lowest being symmetric, the next antisymmetric, etc. The LUMO of **13** is its NBMO (nonbonding MO) which is symmetric if *n* is odd and antisymmetric if *n* is even.[26a] The two situations are indicated in Figure 5b,c.

Since the methyl AO is empty, the energy of union (ΔE_u) arises from interactions between it and the filled MOs of **13**. The corresponding second-order perturbations are given by:[26b]

$$\Delta E_{11}{}^{\text{II}} = 2\sum_{\mu}^{\text{B}}(a_{\mu r}{}^2)/E_\mu \tag{3}$$

$$\Delta E_{12}{}^{\text{II}} = 2\sum_{\mu}^{\text{B}}(a_{\mu r} + a_{\mu s})^2/E_\mu \tag{4}$$

In union to form **11**, all the interactions contribute. In union to form **12**, those interactions involving antisymmetric MOs of **13** vanish but the remaining ones are four times as large. The largest single interaction is expected[26a] to be that between the empty methyl AO and the HOMO of **13**. If the HOMO of **13** is symmetric, which is the case if the parent dication contains 4*m* atoms (*m* being an integer), **12** should then be much more stable than **11**, i.e., aromatic, because the leading term in the second-order expansion is four times as large for **12** as for **11**. If, however, the dication contains (4*m* + 2) atoms, the methyl/HOMO interaction vanishes in **12**. However, the next term in the second-order expression, corresponding to an interaction between the methyl AO and the next highest occupied MO of **13**, is four times as large for **12** as for **11**. The net effect cannot be predicted without detailed calculations, but it is likely to be small. Thus while dications with 4*m* atoms should be strongly aromatic, those with (4*m* + 2) atoms should be at most weakly antiaromatic. Similar reasoning shows that the same rule should also hold for dianions, those with 4*m* atoms being strongly aromatic while those with (4*m* + 2) atoms are probably weakly antiaromatic.[29] The experimental evidence certainly supports these conclusions in the sense that numerous diions have been prepared by oxidation or reduction of neutral aromatic hydrocarbons, implying that the destabilization of these antiaromatic species must be quite small.

Why then does MINDO/3 predict **2a** to adopt a chair-type structure (**6a**), with essentially isolated allyl cation units, given that the destabilization of the symmetrical planar isomer **7a** seems likely to be small? The difference in energy between the planar and chair forms (11 kcal/mol) also seems much too large to be attributed to the small further decrease in cyclic conjugation brought about by nonplanarity, particularly since it is gained only at the expense of twisting the CC bonds in each allyl unit. In the case of $C_5H_5{}^+$, where the distortions probably *are* due to antiaromaticity, the planar and nonplanar forms differ in energy by only 1.5 kcal/mol.[15]

Interelectronic repulsions, which are neglected in simple one-electron MO treatments, may well be responsible. In the symmetrical planar form (**7a**) of **2a**, the four π electrons are distributed uniformly around the ring, two-thirds on average at each atom. In allyl cation **14**, however, according to HMO theory, there is an average of one electron at each central carbon atom and one-half of one electron at each other carbon, while in a SCF–MO treatment the concentration of electrons on the central atom is predicted to be still greater.[30] The uncoupling of the allyl units in **7a** therefore serves to keep the pairs of π electrons as far apart from one another as possible, thus reducing the repulsions between them. Note that the same effect holds even if the molecule is planar: the geometry calculated for **7a** shows a similar fragmentation into allyl units, as indicated in **15a**.

The concentration of charge on the central allylic carbon atoms can be further accentuated by twisting the CC bonds in each allyl moiety, thus decreasing the π interactions in it. This can be achieved by bending **7a**, i.e., by converting it to **6a**. Bending it in the opposite direction, into a boat, would be less favorable because it would bring the central atoms in the allyl units closer together.

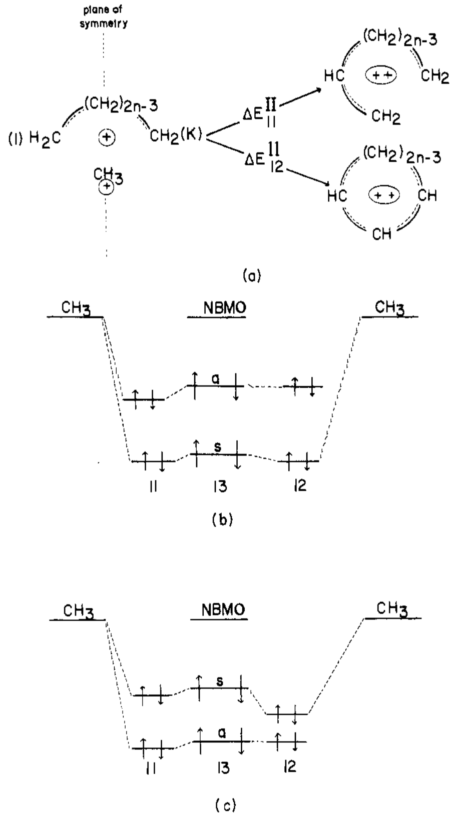

Figure 5. PMO treatment of cyclic diions: (a) union of methyl cation with an odd (2*n* – 1)-atom AH cation; orbital interactions involved (b) when *n* is odd and (c) when *n* is even.

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[29] While this argument applies only to monocyclic ions, it can easily be extended to polycyclic ones by using the previous approach[27] for neutral and singly charged polycyclic systems.

[30] See ref 21, section 5.11.

Table V. MINDO/3 Charges for Singlet Chair Species, **6a–e**

	6a	6b	6c	6d	6e
C_1	0.22	0.07	0.26	0.20	0.16
C_2	0.02	0.40	0.04	-0.01	0.59
C_3	0.23	0.11	0.25	0.18	0.33
C_4	0.22	0.09	0.25	0.18	0.17
C_5	0.03	0.40	0.05	-0.01	0.58
C_6	0.23	0.12	0.24	0.19	0.34
R_1	0.17	-0.92	0.17	0.22	-0.02
R_2	0.18	-0.77	0.12	0.19	-0.02
R_3	0.17	-0.91	0.17	0.22	-0.04
R_4	0.18	-0.91	0.16	0.23	-0.02
R_5	0.17	-0.77	0.12	0.18	-0.03
R_6	0.17	-0.90	0.16	0.23	-0.03

This argument is supported by a comparison of the geometries calculated for **6a** and **14**. The four "allylic" bonds in **6a** are longer by 0.02 Å and the C–C–C bond angle is smaller (108° vs. 127°) than in **14**. Since the π electrons in **14** are concentrated mainly on the central carbon atom, where the formal positive charge is consequently smallest, the repulsion between the pairs of allylic electrons in **7a** leads in effect to a repulsion between the carbon atoms marked with asterisks in **15a**. Such a repulsion would be expected to stretch the CC bonds, and to reduce the CCC bond angles.

All five ions (**2**) were found to have stable chair-type isomers. Table I shows their calculated energies while Tables IV and V indicate the corresponding geometries and distributions of formal charge.

The pyramidal (**3a**) and chair (**6a**) forms of the parent ion are predicted to have almost identical energies, in agreement with the earlier MINDO/3 calculations.[7c] The same is true for the hexamethyl derivatives, **3d** and **6d**. The other three substituents (O, Cl, F) stabilize the chair isomers (**6b**, **6c**, **6e**) relative to the pyramidal isomers (**3b**, **3c**, **3e**) by 42, 23.5, and 44 kcal/mol, respectively. In fact, experimental evidence for a pyramidal isomer has been reported only in the case of **2d**.[8]

The parallel between **3a**/**6a** and **3d**/**6d** suggests that the primary effect of methyl is inductive.[31] A purely inductive substituent, if introduced in place of hydrogen at *every* position in **3a** or **6a**, should alter their energies by the same amount. For the same reason, the inductive effects of other substituents should lead to similar changes in the energies of both isomers. Any differences between the two must then be attributed to electromeric (conjugative) effects.

A $-E$ substituent should stabilize **6a** more than **3a** because the carbon atoms in **6a** form parts of semilocalized allyl cations whereas those in **3a** are involved in a quasisaturated network.[7] Since O, Cl, and F can all exert $-E$ effects, because of their unshared electron pairs,[23] these substituents would be predicted to selectively stabilize the chair isomer.

As mentioned previously, the D_{6h} form of **2a** is expected to undergo Jahn–Teller distortion to one of the structures indicated in **15a** and **16a**. Clearly **6a** corresponds to **15a**, the coupling between the allyl moieties being further weakened in **6a** by distortion from planarity (cf. **1**[15]). Intuition would suggest that the alternative (**16**) should be preferred in the case of **7b** because it is possible to write a reasonable classical structure (**17**) for it. Our calculations support this intuition, the bonds in the "allyl" moieties in **6b** being long (1.50 Å) while the bonds linking them are short (1.41 Å).

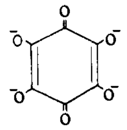
Since the LUMO of the allyl cation is a NBMO (nonbonding MO) and since the interaction between the allyl units in **6a** leads to a first-order splitting of each level, the LUMO of **6a** is a bonding MO, excitation to which should require less energy than excitation to an antibonding MO, as in **3a**. The calculated singlet–triplet splittings (Table I) are indeed so small as to suggest that the singlet and triplet forms of **2a–e** differ little in energy. The experimental evidence is consistent with this suggestion, **2d** having been obtained as singlet **3d** and **2c** as a ground-state triplet.

Although the triplet forms of **2** might be expected to have D_{6h} symmetry, since the two degenerate HOMOs of benzene are each singly occupied in the triplet, we found that the chair triplet form of **2a** is a minimum on the potential surface and the chair forms of triplet **2b–e** were predicted to be likewise stable species. Their stability can only be due to the effects of electron repulsion, confirming our interpretation of the singlet structures.

The energies and geometries calculated for triplet **6a–e** are shown in Tables I and IV, respectively. The geometries are quite close to those of the chair singlets, indicating their common origin.

C. **Conversion of Pyramid to Chair**. The conversions of **3a** to **6a** and of **3d** to **6d** were next studied. Since MINDO/3 predicts both rearrangements to be almost thermoneutral, the barriers to interconversion are the same in both directions: 31 kcal/mol for **3a** to **6a** and 16 kcal/mol for **3d** to **6d**. The experimental evidence[8] indicates that either (a) the barrier for conversion of **3d** to **6d** is greater than 21.5 kcal/mol or (b) **6d** must be less stable than **3d** by at least this amount. The latter possibility would imply errors in the MINDO/3 heats of formation that seem improbably large, judging by calculations for other carbocations.[12,14] It is, however, quite possible for activation energies calculated by MINDO/3 to be in error by 10 kcal/mol. The failure of **3d** to rearrange is therefore probably kinetic in origin and the reverse reaction also comparably slow. If so, it should be possible to prepare **6d** as a relatively stable species from an appropriate monocyclic precursor. Both isomers (**1** and **18**) of $(CH)_5^+$ are known.[15]

D. **Planar Ions**. The analogous ion, $(CH)_5^+$, exists[15] only as the pyramid (**1**) and the nonplanar monocyclic species (**18**). The planar ion distorts to **18** without activation because this reduces its antiaromaticity. However, the planar forms (**7**) of *all* the derivatives (**2**) of **2a** were found to be stable species. Their calculated energies, geometries, and distributions of formal charge are shown in Tables I, VI, and VII, respectively.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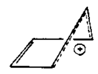
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The bond lengths and charge distributions in **7a,c–e** were similar to those in the analogous chair isomers (**6a,c–e**), demonstrating the relationship discussed above in the case of **2**. The structure of the fifth planar species (**7b**) was different from those of the others for reasons indicated previously.

The triplet forms of all five ions also formed stable planar isomers (**7**); their energies are shown in Table I. Although the planar triplets might be expected to have D_{6h} symmetry, since they are effectively aromatic, the calculated bond lengths in them were unequal. The resulting structures are quite different from those of the planar singlets, i.e., allyl-type units linked by relatively long CC bonds.

Even more surprising is the fact that four of the triplet chair isomers (**6a–d**) are predicted to be more stable than the corresponding planar ones (**7a–d**), while the fifth (**6e**) is only marginally less stable. The stability of the triplet chair isomers, and their geometries, may be attributed to electron repulsions of the kind considered in our discussion of the chair singlets. In the planar triplets the effects of aromaticity evidently just balance the electron repulsions, leading to geometries which neither have D_{6h} symmetry nor can be dissected into pairs of allyl-like units.

Although the ESR evidence[8] shows **2c** to be a ground-state triplet with D_{6h} symmetry, contrary to the MINDO/3 prediction that triplet **2c** is most stable in the chair form (**6c**), the difference between the energies calculated for **6c** and **7c** is very small (2 kcal/mol). According to the arguments given above, both the stability of **6c** and the loss of symmetry in the planar triplet (**7c**) are due to interelectronic repulsions. Thus, the experimental results imply that MINDO/3 slightly overestimates their effects.

E. **Boat Isomer**. The only other monocyclic isomer found for these species was a boat form (**20**) of the hexaoxyion, **2b**. Thus, **2b** is unique in forming *four* distinct stable monocyclic isomers,

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(31) Libit, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1974**, *96*, 1370.

Table VI. MINDO/3 Optimized Geometries (Distances in Å, Angles in deg) of Singlet and Triplet Planar Species, **7a–e**

species		r_1	r_2	r_3	r_4	$C_1C_2C_3$	$C_2C_3C_4$
7a	singlet	1.405	1.47	1.11	1.10	112.7	123.6
	triplet	1.43	1.43	1.11	1.11	119.5	120.3
7b	singlet	1.535	1.41	1.33	1.25	119.6	120.9
	triplet[a]	1.50	1.485	1.30	1.295	120.5	120.5
7c	singlet	1.415	1.52	1.695	1.74	119.2	120.4
	triplet[a]	1.45	1.44	1.71	1.71	120.5	120.5
7d	singlet	1.52	1.40	1.51	1.47	120.8	119.5
	triplet[a]	1.48	1.47	1.49	1.48	120.4	120.5
7e	singlet	1.48	1.37	1.35	1.30	120.3	119.7
	triplet[a]	1.44	1.445	1.335	1.33	120.5	120.5

[a] The calculated geometry showed small irregular variations from the D_{2h} symmetry exhibited isomers. The values listed are averages for bonds and angles that would be equal under D_{2h} symmetry.

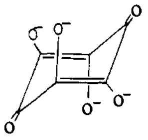
Table VII. MINDO/3 Charges for Singlet and Triplet Planar Species, **7a–e**

compound		C_1	C_2	R_1	R_2
7a	singlet	0.4	0.02	0.16	0.18
	triplet	0.17	0.18	0.16	0.16
7b	singlet	0.09	0.38	-0.91	-0.75
	triplet[a]	0.16	0.20	-0.84	-0.83
7c	singlet	0.29	-0.01	0.18	0.09
	triplet	0.17	0.20	0.15	0.15
7d	singlet	0.02	0.36	0.18	0.38
	triplet	0.13	0.14	0.20	0.20
7e	singlet	0.23	0.62	-0.03	-0.02
	triplet	0.36	0.36	-0.02	-0.03

[a] The charges on all triplet species except the parent, **7a**, are average values due to the irregularity of geometry mentioned in Table VI.

3b, **6b**, **7b**, and **20**. The boat isomer (**20**) was the most stable of the four, being indeed the most stable form of the $(CO)_6^{4-}$ ion. The bond lengths calculated for **20** are shown in Table IV and the formal charges in Table VIII.

Since **2b** alone has a reasonable classical structure (**17**) corresponding to the second Jahn–Teller distorted geometry (**16**), it is not surprising that it is the only species to form a stable isomer of this type. According to this representation, **2b** can be regarded as a (tetraoxy) derivative of boat *p*-benzoquinone, **21**. Since a chair form of benzoquinone would be highly strained, the chair isomer (**19**) of **2b** is understandably less stable than **20**.



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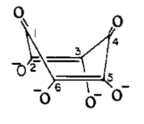

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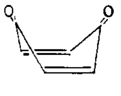

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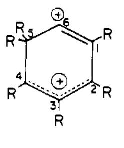

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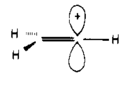

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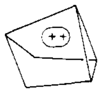

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F. Other Isomers. During our attempts to follow the conversions of **3a** to **6a**, we found another minimum on the potential surface, corresponding to a species best represented as **22a**. This is derived from **6a** by migration of hydrogen, effectively converting one of the allyl cation units in **6a** to a vinyl cation. A similar isomer (**22d**) of **2d** was also found to be a minimum on the corresponding potential surface. The heats of formation calculated for **22a** and **22d** are shown in Table I, their geometries in Figure 6, and the distributions of formal charge in Table VIII.

Table VIII. MINDO/3 Charges for Other Singlet Dications

	22a	**22b**	**20**
C_1	-0.05	0.01	0.42
C_2	0.35	0.30	0.12
C_3	-0.11	-0.12	0.06
C_4	0.29	0.26	0.42
C_5	-0.08	0.01	0.09
C_6	0.48	0.30	0.09
R_1	0.24	0.26	-0.77
R_2	0.14	0.23	-0.91
R_3	0.19	0.24	-0.92
R_4	0.14	0.21	-0.77
R_5	0.20	0.18	-0.92
R_6	0.20	0.18	-0.91

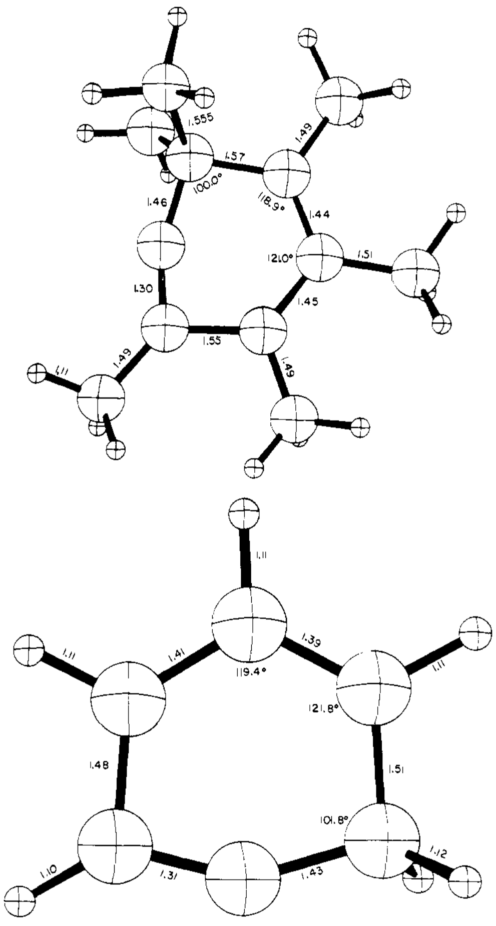

Figure 6. Geometries calculated for **22a** (top) and **22d** (bottom).

In the unsubstituted system, this isomer (**22a**) is predicted to be lower in energy, by 5 kcal/mol, than either the pyramid (**3a**) or the chair (**6a**), while in the hexamethyl series the new isomer (**22d**) is predicted to be higher in energy than either **3d** or **6d**. MINDO/3, however, seems to overestimate the stabilities of unsaturated carbocations. In particular, it predicts the 2-propenyl

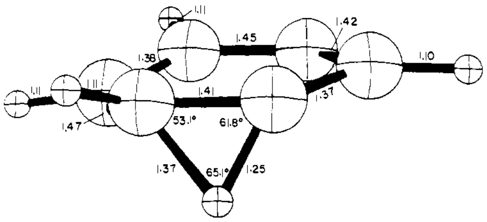

Figure 7. Transition state for the 1,2-H shift in **6a** to form **22a**.

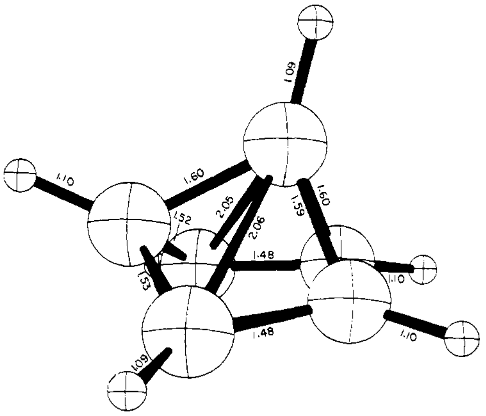

Figure 8. MNDO puckered pyramid, **24**.

cation (**23**) to be more stable than the allyl cation (**14**), by 8.6 kcal/mol, whereas it is in fact less stable by 11 kcal/mol.[32] It therefore seems very likely that **22a** is less stable than the pyramidal (**3a**) or chair (**6a**) isomers.

The formation of **22** from **6a** would be expected to involve a 1,2 shift of hydrogen. Which hydrogen and to which adjacent position are not, however, obvious, given that **22** is planar. Taking an H–C–C angle as the reaction coordinate, all possible hydrogen migrations were found to give similar activation energies of 17 ± 1 kcal/mol. This activation energy is greater than those calculated for rearrangements of carbenium ions, many of which are less stable than the corresponding olefin–proton π complexes. Figure 7 portrays a typical transition state, which was only slightly unsymmetrical.

G. Ground-State Multiplicity. As Table I shows, there are only small predicted energy differences between the lowest singlet and lowest triplet forms of these ions. One would normally expect, then, that they would all have singlet ground states, since UMINDO/3 usually gives triplet energies that are too negative, due to an overestimation of the correlation energy.[33] However, a recent extensive MNDO study[34] of triplet states has shown that the errors can vary from 0 to 30 kcal/mol, depending on the type of molecule in question. The errors are systematic, so the relative magnitudes of singlet–triplet splittings for molecules of the same kind are reproduced satisfactorily. Because the errors in triplet calculations with UMINDO/3 and UMNDO have a common cause, the UMINDO/3 singlet–triplet splittings for the ions considered here should be more or less correct. The energies of the triplets, relative to the singlets, for **2a**, **2b**, **2c**, **2d**, and **2e** are calculated (Table I) to be 2.5, -1, -3.5, -1.3, and -6 kcal/mol, respectively. Those with the least stable triplets are **2a**, **2b**, and **2d**, two of which are known to have singlet ground states,[8,10] while the ground state of **2c** is known[8] to be a triplet. Our calculations, and the experimental results for **2c**, allow a fairly confident prediction that the hexafluoro ion (**2e**) will also prove to have a triplet ground state.

Table IX. MNDO RHF Results

compd	ΔH_f, kcal/mol	compd	ΔH_f, kcal/mol
3a	649.2[a,b]	**24**	641.6
6a	578.0[b]	**25**	605.7
15a	577.8[c]		

[a] This structure corresponds to the top of a hill on the potential surface, not a minimum. It is a stationary point but its Hessian (force constant) matrix has two negative eigenvalues. The other species listed in this table do correspond to minima on the potential surface. [b] These values agree with those reported by Lammertsma and Schleyer.[7c] [c] The heat of formation of the UHF planar triplet is 571 kcal/mol, also in agreement with the value reported by Lammertsma and Schleyer.[7c]

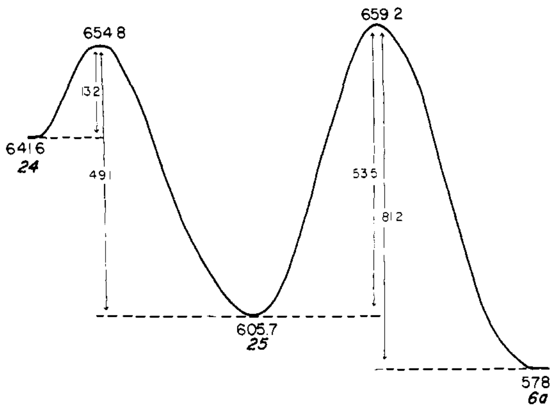

Figure 9. MERP for conversion of **24** to **6a**. Energies are given in kcal/mol.

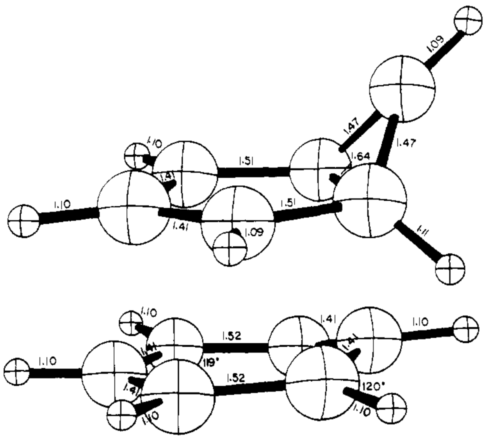

Figure 10. MNDO geometries calculated for **25** (top) and **6a** (bottom).

MNDO Calculations

Since Lammertsma and Schleyer[7] have arrived at conclusions somewhat different from those presented here, on the basis of MNDO and ab initio calculations, we thought it would be of interest to check their MNDO results. Our MNDO calculations for $C_6H_6^{2+}$ in fact differ in several significant respects from theirs.

In the first place, the symmetrical pyramidal ion, **3a**, is *not* a minimum on the MNDO potential surface. On the contrary, its Hessian (force constant) matrix has *two* negative eigenvalues, implying that it is in fact the top of a hill. The energy we calculate for it agrees well with that reported by Lammertsma and Schleyer. The true minimum is a puckered pyramid (**24**) whose geometry is indicated in Figure 8. The symmetrical structure (**3a**) has two negative force constants because it can be distorted in either of two orthogonal directions to form **24**. The symmetrical pyramid (**3a**) is higher in energy than the puckered pyramid (**24**) by 7.6 kcal/mol. The MNDO heats of formation for **3a** and **24** are shown in Table IX.

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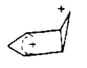
[32] (a) Aue, D. H.; Davidson, W. R.; Bowers, M. T. *J. Am. Chem. Soc.* **1979**, *101*, 4681. (b) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *Ibid.* **1981**, *103*, 5649.

[33] In MINDO/3 and MNDO, allowance is made for electron correlation via the parametrization, thus providing in effect an averaged correction. In UHF treatments of biradicals and triplets, specific allowance is made for the correlation between the "unpaired" electrons. Use of the regular MINDO/3 or MNDO parameters in such cases, therefore, leads to an overestimation of the correlation energy.

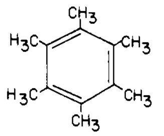
[34] Dewar, M. J. S.; Fox, M. A.; Campbell, K. A.; Chen, C.-C.; Friedheim, J. E.; Holloway, M. K.; Kim, S. C.; Liescheski, P. B.; Pakiari, A. M.; Tien, T.-P.; Zoebisch, E. G. *J. Comput. Chem.*, in press.

Our energy for the chair isomer (**6a**) again agrees with the reported value. However, the planar isomer (**7a**) is also a minimum on the MNDO potential surface, as it was in the case of MINDO/3. While the difference in energy between **6a** and **7a** was only 0.2 kcal/mol, their calculated force constants showed that *both* are true minima.

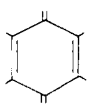
We also found a fourth stable isomer on the MNDO surface, i.e., the bicyclo[3,1]hexen-3,5-diyl dication (**25**), this being a stable intermediate on the minimum-energy reaction path (MERP) for conversion of **24** to **6a** (see Figure 9). The geometries of these species are shown in Figure 10. As noted above, no minimum corresponding to **25** could be found on the MINDO/3 potential surface.



25



26



27

These results support our contention that MINDO/3 is likely to give better accounts of systems of this kind than MNDO. There is certainly no evidence for the existence of minima on the potential surface corresponding either to the unsymmetrical pyramidal structure, **24**, or to the bicyclic ion, **25**. Here, as elsewhere, MNDO seems to underestimate the stabilities of "nonclassical" species, a conclusion reached previously from detailed studies of numerous boron hydrides and carboranes.[35,36]

Summary and Conclusions

The calculations reported here seem to provide a very satisfactory picture of the potential surfaces for the benzene dication and for four of its hexasubstituted derivatives, the substituents being O^-, Cl, CH_3, and F. Three stable singlet isomers were predicted for each ion: (a) a pentagonal pyramid (**3**) with C_{5v} symmetry (distorted in the case of the hexaoxy ion); (b) a nonplanar monocyclic species (**6**) with a geometry analogous to that of chair cyclohexane; and (c) a monocyclic planar species (**7**). The hexaoxy isomer is unique in also forming a fourth stable monocyclic species, **20**, analogous to boat cyclohexane.

The calculations suggest that all these ions may have low-lying triplets or even exist as ground-state triplets. The experimental evidence supports this conclusion, **2d** having been obtained in the form of singlet **3d**, while **2c** is a ground-state triplet.

The pyramidal and chair forms of the parent ion (**3a**, **6a**), and of its hexamethyl derivative (**3d**, **6d**), are predicted to have similar heats of formation, the isomers being separated by significant activation barriers (31 and 16 kcal/mol, respectively). Although the NMR evidence for the hexamethyl isomer[8] indicates that the barrier to rearrangement must be higher than that calculated, it should be possible to obtain the chair isomer (**6d**) as a reasonably stable species in matrices or solution by starting with a suitable monocyclic precursor. Possible routes would be oxidation of hexamethylbenzene (**26**) or protonation of duroquindimethane (**27**).

Our calculations make attempts to prepare pyramidal isomers (**3c** and **3e**) of the hexachloro and hexafluoro ions seem unattractive, as they are predicted to be very much higher in energy than the singlet chair isomers, which in turn are predicted to be less stable than the corresponding triplets. Preparation of the pyramidal isomer (**3b**) of the hexaoxy ion may be a little easier. However, if **3b** exhibits the predicted distortion from C_{5v} symmetry, there would not be much point in making it.

Our discussion of these ions in terms of simple MO theory accounts well for the large calculated variations in the relative energies of the various isomers. These lead to a clear prediction that stable pyramidal ions should be obtainable only if the substituents in them are incapable of electromeric electron release. A further interesting conclusion is that in an ion carrying six identical substituents, the relative energies of the pyramidal (**3**) and chair (**6**) isomers should be unaffected by inductive/field effects of the substituents. This could lead to a novel and possibly effective method for distinguishing between them and effects due purely to π-conjugation. Our results, interpreted in this way, confirm (a) that electron release by methyl does not involve π-conjugation[31] and suggest (b) that the $-E$ effects of O^- and F are similar, the greater electron release by the former being primarily electrostatic in nature. The $-E$ effect of Cl is, as expected, much less.

It has been generally assumed in the past that the benzene dication is antiaromatic, having four π electrons. This, however, involves a wholly unjustified extrapolation of Hückel's rule. The PMO argument given here shows that while dications or dianions with $(4n + 2)$ π electrons should be strongly aromatic, as indeed is known to be the case, those with $4n$ π electrons should be at most weakly antiaromatic. The distortion of the monocyclic singlet dications from D_{6h} symmetry seems indeed to be due to interelectronic repulsions rather than to antiaromaticity, because similar distortions are also predicted in the corresponding triplet which is not antiaromatic. The fact that the hexachloro (**2c**) and hexafluoro (**2e**) ions are predicted to exist as stable planar singlets, **7c** and **7e**, similar in energy to the analogous chair isomers (**6c** and **6e**), again suggests that antiaromaticity does not play a major role.

Our results also indicate very clearly that the monocyclic hexaoxy ion is *not* aromatic, as has been suggested. It is better regarded as a derivative of *p*-benzoquinone.

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(35) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1978**, *17*, 1569.

(36) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1980**, *19*, 2662.