the lanthanide–lasalocid interactions. Although of no *direct* physiological interest, Tb^{3+} should prove to be an excellent spectroscopic replacement probe for the physiologically ubiquitous Ca^{2+} ions in studies devoted to Ca^{2+}–lasalocid complexation and transport.

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The Potential Surface for the Cyclobutadiene Radical Cation

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Abstract: Ab initio calculations on the cyclobutadiene radical cation have been carried out with an STO-3G basis set. At a square geometry the RHF, UHF, and π CI energies all depend on whether rectangular or rhomboidal D_{2h} symmetry is imposed on the wave function. The reasons for this undesirable dependency are discussed, and it is shown that inclusion of CI in both the σ and the π space is necessary to remove it. σ–π CI calculations have been used to determine the optimal rectangular (b_{1g}) and rhomboidal (b_{2g}) molecular distortions, which are predicted by the Jahn–Teller theorem to result in first-order energy lowering. A rectangular structure is found to correspond to the two minima on the potential surface and a rhomboidal structure to the two transition states, 6.0 kcal/mol higher in energy, that connect the minima. It is shown that, unlike the tetra-*tert*-butyl derivative of cyclobutadiene, the corresponding derivative of the radical cation will not have almost equal bond lengths. Other differences between the neutral molecule and the radical cation are discussed.

Ab initio molecular orbital (MO) theory has proven successful in predicting[1-4] the rectangular equilibrium geometry of cyclobutadiene[5,6] and rationalizing[7] the nearly square geometry of the tetra-*tert*-butyl derivative.[8] In this paper we report the results of calculations on the radical cation of cyclobutadiene.

Two groups have published EPR spectra of tetraalkyl derivatives of the parent radical cation.[9,10] In both cases the hyperfine splitting observed indicated the equivalency on the EPR time scale of all four alkyl groups. This finding is consistent with, but does not demand, an equilibrium geometry in which the four ring carbons are equivalent by symmetry. One of the goals of our theoretical study was to predict the structure of the parent radical cation and, by inference, those of the tetraalkyl derivatives whose EPR spectra have been obtained.

Another objective of this work was to explore the minimal requirements for satisfactory wave functions for the radical cation of cyclobutadiene. Our theoretical studies of diradicals[11] have demonstrated both the importance and the difficulty of obtaining satisfactory wave functions when two electrons must be placed in degenerate or nearly degenerate orbitals. The results of the present study reveal that similar types of problems arise when the degenerate π orbitals of square cyclobutadiene are occupied by a single electron.[12]

Theoretical Considerations

The Jahn-Teller Theorem[13] predicts that the lowest state (^2E_g) of the cyclobutadiene radical cation will distort from a square geometry. First-order energy lowering is predicted along b_{1g} and b_{2g} distortion coordinates. The former transforms the square molecule to a rectangle; the latter affords a rhombus.

Since the two distortions are not degenerate, there is no reason to anticipate that they will produce identical energy lowering. In fact, one distortion is expected to lead to two equivalent minima on the potential surface for the lowest state, while the other should lead to two equivalent transition states connecting the minima.[14] The radical cation is therefore expected to pseudorotate about a square geometry, as illustrated in Figure 1. The energy difference between the stationary points along the b_{1g} and b_{2g} coordinates is equal to the energy required for the pseudorotation process.

Optimizing the geometries along the rectangular and rhomboidal distortion coordinates requires calculations in two different D_{2h} subgroups of D_{4h}, the point group to which the square molecule belongs. Consequently, two different sets of degenerate (e_g) MO's are required for following the b_{1g} and b_{2g} distortions from D_{4h} symmetry. These MO's are shown schematically in Figure 2. At a D_{4h} geometry it should be possible to use either set, since they are related by an orthogonal linear transformation.[15] However, as discussed below, at some levels of calculation the energy will,

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[2] Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1977**, *99*, 3583.

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[8] Irngartinger, H.; Rieglere, N.; Malsch, K. D.; Schneider, K. A.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 211.

[9] Bock, H.; Roth, B.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 209.

[10] Broxterman, Q. B.; Hogeveen, H.; Kok, D. M. *Tetrahedron Lett.* **1981**, *22*, 173.

[11] Review: Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1981**, *14*, 69.

[12] The problems encountered in calculations on the isoelectronic cyclopropenyl radical are related in a general way to those discussed here but differ in detail because of the differences in symmetry and charge between the two systems. The difficulties that arise in the cyclopropenyl radical are discussed in: Davidson, E. R.; Borden, W. T. *J. Chem. Phys.* **1977**, *67*, 2191. See also: Poppinger, D.; Radom, L.; Vincent, M. A. *Chem. Phys.* **1977**, *23*, 437.

[13] Jahn, H. A.; Teller, E. *Proc. R. Soc. London, Ser. A* **1937**, *161*, 220.

[14] See, for instance, the potential surface that appears in: Herzberg, G. "Molecular Spectra and Molecular Structure"; Van Nostrand: New York, 1966; p vol. 3, 44.

[15] Actually, there are infinitely many sets of degenerate MO's that should each give the same energy at a D_{4h} geometry, since each can be expressed as a linear combination of either the rectangular or rhomboidal set. Choice of the appropriate linear combination will result in MO's that are unmixed by a given combination of rectangular and rhomboidal distortions.

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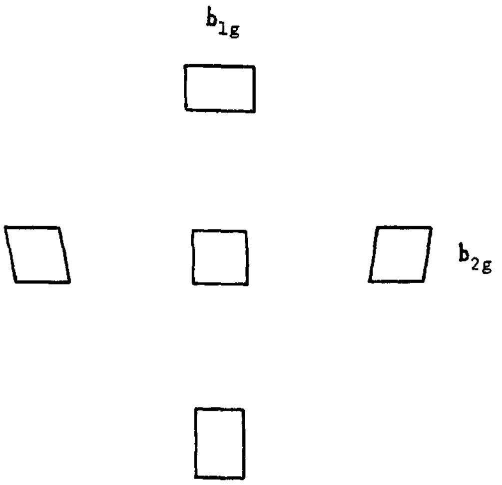

Figure 1. Pseudorotation in the cyclobutadiene radical cation.

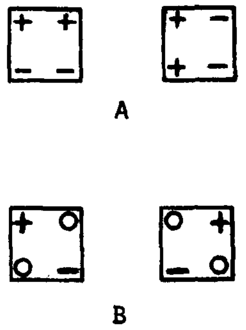

Figure 2. Schematic depiction of the degenerate π (e_g) MO's in cyclobutadiene with (A) rectangular and (B) rhomboidal D_{2h} symmetry.

in fact, depend on the supposedly arbitrary choice of nonbonding MO's.

With D_{4h} symmetry MO's the lowest energy electronic configuration of square cyclobutadiene is $|\ldots a_{2u}{}^2\, e_g\rangle$, where a_{2u} is the bonding π MO. It can be shown that this configuration does not satisfy Brillouin's theorem for open-shell systems,[16] since another configuration of E_g symmetry can be constructed by a single excitation from a_{2u} to b_{1u}, where the latter MO is the antibonding π orbital with nodes between each of the adjacent carbons. Therefore, a lower SCF energy can be obtained if mixing of a_{2u} and b_{1u} is allowed. In order for this mixing to occur, D_{4h} symmetry must not be imposed on the SCF wave function.

Interestingly, even if only rectangular D_{2h} symmetry is imposed on the wave function, the two relevant MO's still belong to different representations (b_{3u} and a_u) of this point group. However, if rhomboidal D_{2h} symmetry is imposed, both MO's belong to b_{3u}; and so they can mix. Therefore, it is to be expected that, at a D_{4h} geometry, carrying out a calculation in the rhomboidal D_{2h} subgroup will lead to a lower SCF energy than imposition of rectangular D_{2h} symmetry on the wave function.

There is a simple physical reason for this anomaly. When rhomboidal symmetry is imposed, the odd electron occupies an MO with density at only two carbons, which lie along one diagonal plane of symmetry. Electron repulsion can then be minimized by allowing the electrons in the lowest π MO to appear with unequal probabilities at the two sets of carbons along the diagonal planes. This is what results from the mixing of the a_{2u} and b_{1u} D_{4h} symmetry orbitals.

When rectangular symmetry is imposed, however, the odd electron appears with equal probability at all four carbon atoms. Consequently, the electron repulsion energy cannot be reduced at the SCF level by the same type of mechanism that is possible when the symmetry imposed is rhomboidal. With the imposition of rectangular D_{2h} symmetry, mixing of the lowest configuration with a doubly excited one[17] is required to recover this type of electron correlation energy.

It might be hoped that by carrying out configuration interaction (CI) among all possible π configurations, the MO's obtained from rectangular and rhomboidal SCF calculations would yield the same CI energies. The success of a full π space CI approach is predicated, however, on the same charge distribution in the σ core emerging from both sets of SCF calculations. That this is unlikely to be the case can be inferred from the physical argument, given above, as to why the lowest π MO from the rhomboidal D_{2h} calculation should differ from the corresponding MO obtained from the rectangular D_{2h} calculation. Once again the rhomboidal calculations should yield the lower energy, since it allows the σ SCF wave function to respond to a nonuniform distribution of π charge, thus producing a lower σ–π Coulombic repulsion energy than when rectangular D_{2h} symmetry is imposed.

Several strategies are possible for dealing with the unhappy dependence of the energy calculated at a D_{4h} geometry on the choice of the D_{2h} subgroup in which the calculation is carried out. One possibility is to perform all the calculations on the cyclobutadiene cation radical in the C_{2h} subgroup that is common to both the rhomboidal and the rectangular D_{2h} point groups. However, with only C_{2h} symmetry imposed, it is verly likely that at some rectangular D_{2h} geometries the wave function will not have the full molecular symmetry, because a set of MO's with rhomboidal symmetry gives a lower Coulombic repulsion energy.

Another possible approach is based on the fact that each of the e_g MO's with rectangular D_{2h} symmetry can be expressed as a linear combination of the e_g MO's with rhomboidal D_{2h} symmetry. Similarly, it ought to be possible at D_{4h} geometries to write a wave function with D_{2h} rectangular symmetry as a linear combination of two configurations, each of which has D_{2h} rhomboidal symmetry. Since the two configurations would have the same energy and be noninteracting at D_{4h} geometries, the resulting wave function, with rectangular D_{2h} symmetry, would be guaranteed to have the same energy as each of rhomboidal SCF wave functions from which it was built. More generally, at any D_{2h} geometry a two-configuration wave function of the same symmetry could be produced as a linear combination of a C_{2h} SCF wave function and a second configuration, obtained by reflecting the SCF MO's through one of the D_{2h} symmetry planes that is orthogonal to the molecular plane.

The problem with this approach would come from the fact that, in general, none of the MO's in the two configurations would be the same, nor would they be orthogonal to each other. Since most computer programs only handle orthonormal MO's, the C_{2h} MO's in the two-configuration wave function would have to be written as linear combinations of a common set of MO's with D_{2h} symmetry. When written in terms of orthonormal D_{2h} MO's, the two-configuration wave function would become multiconfigurational, containing terms representing excitations in both the σ and π space from the dominant configuration.

We chose to take another approach to obtaining such a multiconfiguration wave function. Our prevoius work on diradicals has shown that CI involving all single excitations in the σ valence space for all possible π configurations represents a satisfactory method for obtaining wave functions when the σ core is affected by a nonuniform distribution of π charge. In calculations on the cyclobutadiene radical where the wave function is forced to have rectangular D_{2h} symmetry, this type of CI apprach should allow the recovery of σ–π correlation energy, part of which is obtained at the SCF level when D_{2h} rhomboidal symmetry is imposed. Consequently, with this type of CI the same or very similar energies should be computed at D_{4h} geometries, independent of which type of D_{2h} symmetry is imposed on the wave function.

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(16) Manne, R. *Mol. Phys.* **1972**, *24*, 935.

(17) The appropriate double excitation from $|b_{3u}{}^2 b_{2g}\rangle$ involves removing an electron simultaneously from b_{3u} and b_{2g} and placing one in a_u and the other in the second nonbonding (b_{1g}) MO. One effect of this excitation is to mix the b_{2g} and b_{1g} MO's, giving another nonbonding MO, but one which has rhomboidal instead of rectangular D_{2h} symmetry. Simultaneously, b_{3u} and a_u are mixed. This is, as discussed in the text, the mixing that occurs when rhomboidal D_{2h} symmetry is imposed on the wave function.

Table I. Results of Calculations at a D_{4h} Geometry with r_{C-C} = 1.45 Å and Two Different Types of D_{2h} Symmetry Imposed on the Wave Function[a]

calculation	rectangular	rhomboidal	ΔE, hartree
RHF	−151.5493	−151.5611	0.0118
UHF	−151.5500	−151.5831	0.0331
π CI	−151.6037	−151.6113	0.0076
σ–π CI	−151.6933	−151.6924	−0.0009

[a] With D_{4h} symmetry imposed on the wave function the energy was higher by 0.0001 hartree at the RHF and π CI levels than when rectangular D_{2h} symmetry was imposed.

Results and Discussion

Calculations were carried out with a basis set of STO-3G orbitals.[18] Previous results on the cyclobutadiene[3] and other hydrocarbon diradicals[11] have shown STO-3G to give energy differences comparable to those obtained with more elaborate basis sets.[19] As in our calculations on cyclobutadiene, the C–H bond lengths in the radical cation were fixed at 1.10 Å, and these bonds were assumed to bisect the C–C–C bond angles.

A series of calculations was first carried out at a D_{4h} geometry with C–C bond lengths of 1.45 Å. The results are shown in Table I for restricted (RHF) and unrestricted (UHF) Hartree–Fock, π space CI, and σ–π CI[20] calculations, with rhomboidal and rectangular D_{2h} symmetry imposed on the wave functions.

At the RHF level the imposition of rhomboidal symmetry gives an energy 7.4 kcal/mol lower than when the wave function is forced to have rectangular symmetry. The lower energy found for the rhomboidal wave function is in accord with the theoretical argument and physical picture given in the previous section. As anticipated, the lowest π MO has unequal coefficients (0.407 vs. 0.424) at the two sets of carbons along the two diagonal planes. However, quite the reverse of what might have been expected, the larger coefficients in the lowest π MO belong to the pair of carbons to which the odd electron is localized.

This is a rather surprising result and would seem to lead to an increase in the Coulombic repulsion energy between the odd electron and the pair in the lowest π MO. For the electron in this MO with spin opposite to that of the odd electron, such an increase does occur, since Coulombic interactions between electrons in nearest neighbor p orbitals (γ_{12}) are traded for an equal mixture of one-center (γ_{11}) and cross ring (γ_{13}) repulsions. The $1/r$ dependence of the Coulomb repulsion energy makes $(\gamma_{11} + \gamma_{13})/2 > \gamma_{12}$.

However, for the electron in the lowest π MO with the same spin as that of the unpaired electron, the Pauli principle prohibits the two electrons from appearing simultaneously in the same AO. Therefore, for this electron increased localization to the same pair of carbons as the odd electron is favorable; since nearest neighbor repulsions are traded for those involving atoms across the ring, and $\gamma_{13} < \gamma_{12}$. The atomic orbital coefficients in the lowest π MO indicate that a C–C bond length of 1.45 Å, the latter effect dominates the former;[21] hence the counterintuitive tendency for the lowest π MO to localize at the same carbons to which the unpaired electron is confined.

In a UHF calculation in rhomboidal D_{2h} symmetry, where the MO's for electrons of opposite spin are allowed to differ, only the electron in the lowest π MO with the same spin as the odd electron tends to localize at the pair of carbons to which the latter electron is confined. The electron of opposite spin tends to localize at the other pair of carbons. Therefore, the UHF energy is considerably lower than that obtained with an RHF calculation.

Table II. Optimized Square, Rectangular, and Rhomboidal Geometries Obtained by σ–π CI Calculations[20]

geometry	r_1, Å[a]	r_2, Å[a]	θ, deg[b]	E, hartree
square	1.469	1.469	90.0	−151.6947[c] −151.6937[d]
rectangular	1.525	1.414	90.0	−151.7059[c]
rhomboidal	1.469	1.469	92.2	−151.6953[d]

[a] C–C bond lengths. [b] Largest C–C–C bond angle. [c] Energy computed with rectangular D_{2h} symmetry imposed on the wave function. [d] Energy computed with rhomboidal D_{2h} symmetry imposed on the wave function.

In contrast, if the odd electron is confined to an orbital with rectangular D_{2h} symmetry, this electron appears with equal probability at each carbon. Thus, the rectangular UHF MO's for the two π electrons of lowest energy cannot be "polarized" by the odd electron in the same way that the rhomboidal UHF MO's can. As a result, the UHF and RHF calculations with rectangular symmetry imposed give nearly the same energies. Consequently the UHF energies, obtained with rhomboidal and rectangular symmetry constraints, differ by 20.8 kcal/mol, nearly three times more than the RHF numbers.

At a square geometry the RHF and UHF calculations in rhomboidal D_{2h} symmetry each give a lower energy than the same type of calculation carried out in rectangular D_{2h} symmetry. Thus, RHF and UHF calculations of the equilibrium geometry of the radical cation would be prejudiced by 7.4 and 20.8 kcal/mol, respectively, toward finding the lowest energy geometry to lie along a rhomboidal (b_{2g}) distortion coordinate. This is why, as we have stressed in our work on diradicals,[11] before beginning to explore a potential surface, it is essential to check that two calculations that should give the same energy at the geometry of highest symmetry actually do so.

Inclusion of π CI decreases the energy difference between the calculations with rhomboidal and rectangular symmetry imposed to 4.8 kcal/mol, two thirds of the RHF discrepancy. The π CI difference is still an uncomfortably large one for two energies that ought to be the same. It reflects the difference in the σ cores, which are unaffected by CI in just the π space.

With inclusion of CI in the σ space,[20] as well as as in the π space, the energy difference drops to 0.6 kcal/mol, 8% of the RHF difference. Interestingly, the MO's with rectangular D_{2h} symmetry now provide the better basis for the CI. This result is in keeping with previous experience that the MO's that deviate least from the full molecular symmetry provide the best basis for carrying out σ–π CI calculations of this type.[11]

Having shown that σ–π CI provides wave functions of rhomboidal and rectangular D_{2h} symmetry that yield nearly the same energies at D_{4h} geometries, we investigated distortions along b_{1g} and b_{2g} at this level of theory. The optimal square, rectangular, and rhomboidal geometries found are given in Table II, along with the associated energies. It is apparent that a rectangular distortion is favored over a rhomboidal one. The former results in the an energy drop of 7.0 kcal/mol, whereas the latter is computed to produce only a 1.0-kcal/mol energy lowering, if calculations with the same symmetry constraints are compared.[22]

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(18) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(19) We have found this certainly not to be the case for cycloaddition reactions involving the making and breaking of π bonds to heteroatoms. See: Feller, D.; Borden, W. T.; Davidson, E. R. *J. Comput. Chem.* **1980**, *1*, 158. Feller, D., Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1981**, *103*, 2558.

(20) σ–π is to be taken as the designation for CI involving all single σ valence space excitations for all π configurations based on RHF MO's. In D_{2h} symmetry this prescription resulted in the generation of 709 $^2B_{2g}$ space–spin configurations.

(21) Using STO-3G orbitals, $(\gamma_{11} + 3\gamma_{13})/2$ is actually slightly larger than $2\gamma_{12}$. The contribution of Coulomb repulsion integrals between atoms and the adjacent overlap regions is apparently responsible for tipping the balance in favor of localizing the lowest π MO at the atoms to which the unpaired electron is confined.

(22) *Provided* that calculations whit the same symmetry constraints are compared, the distortions and associated stabilization energies obtained from π CI calculations are very close to the σ–π CI results. The results are similar because, when the π CI calculations with the same D_{2h} symmetry constraints are compared, cancellation of σ–π Coulombic effects occurs. However, there are systems for which this type of approach, comparing the results of calculations with the same symmetry contraints, fails.[11] Moreover, even in the cyclobutadiene radical cation, there exist rectangular D_{2h} geometries at which an SCF solution with less than D_{2h} symmetry is lower in energy than the symmetry constrained one. Around these D_{2h} geometries attempts to investigate geometries of lower symmetry at the π CI level result in an abrupt and discontinuous drop in the energy as the symmetry constraints on the σ orbitals are forced to be relaxed.

We also investigated geometries of the cyclobutadiene radical cation with lower than D_{2h} symmetry, since there are in addition to the b_{1g} and b_{2g} distortions of the square molecule, a degenerate e_u pair. This pair does not give rise to a first-order Jahn-Teller effect for the ^2E_g ground state, but it does allow second-order mixing of ^2E_g with $^2A_{1u}$, $^2A_{2u}$, $^2B_{1u}$, $^2B_{2u}$ excited states. Second-order Jahn-Teller effects have been shown to be important in antiaromatic annulenes in general[11] and in cyclobutadiene in particular.[3,4]

The e_u distortions of a square can be represented as transforming it either into two different trapezoids or two different kites. In both cases the remaining symmetry is C_{2v}, with the C_2 axis bisecting two bonds for the former representation of the e_u distortions and passing through two atoms for the latter. We carried out σ–π CI calculations for two trapezoidal distortions of the rectangular minimum and for two kite distortions of the rhomboidal one. Atomic motions of 0.01 Å along the appropriate coordinates for the two different distortions around each local minimum led to an increase in the energy. Thus, the rectangular geometry does, indeed, represent the two equivalent minima on the potential surface for the planar radical cation, and the rhomboidal geometry corresponds to the two transition states connecting the minima.

We also investigated whether these geometries might be unstable to distortions of the molecule from planarity. The possibility that this might occur was suggested by the computational finding that the cyclobutadiene dication has a nonplanar equilibrium structure, although a planar structure was found for the neutral molecule.[23]

Since molecular distortion from planarity destroys the distinction between σ and π orbitals that we used in our CI protcol, we carried out calculations on the nonplanar molecules at the RHF level. Starting near the rhomboidal transition state with the two hydrogens along the shorter diagonal shifted out of the plane of the rest of the atoms, geometry optimization[24] with C_{2v} symmetry constraints on the wave function converged to give back a planar molecule.

In contrast, starting near the rectangular minimum with the four hydrogens displaced alternately above and below the plane of the carbons, the RHF geometry optimization gave a nonplanar structure of D_2 symmetry.[25] Nevertheless, each carbon was displaced from coplanarity by less than 0.002 Å and each hydrogen by 0.007 Å. Moreover, the RHF energy of this structure was only 0.000003 hartree lower than that of the corresponding planar one with the same bond lengths. Thus, as might have been anticipated from the modest energy lowering, calculated with the STO-3G basis set, for deviation of cyclobutadiene dication from planarity and from the computed preference of the neutral molecule for a planar geometry,[23] ring puckering is not an important mode of stabilization for the radical cation.

The results of our calculations apply, of course, only to the parent radical cation. The tetra-*tert*-butyl derivative[9] almost certainly adopts a distinctly nonplanar ring geometry, since the crystal structure of the tetra-*tert*-butylcyclobutadiene shows the ring in the neutral molecule, containing an additional π electron, to be nonplanar.[8]

The X-ray structure of tetra-*tert*-butylcyclobutadiene also shows the molecule to have nearly equal bond lengths, in contrast to the structures found for two other derivatives[26,27] and to the strongly rectangular geometry predicted by ab initio calculations on the parent molecule.[1-4] Therefore, the question arises as to whether the radical cation of tetra-*tert*-butylcyclobutadiene might also have nearly equal bond lengths.

We have argued that in the neutral molecule steric repulsions between the *tert*-butyl groups on the double bonds cause lengthening of these bonds and that this process is accompanied by single bond shortening, leading toward a square geometry.[7,28] The preferential coupling of these bond length changes of opposite sign is revealed by MO calculations on the parent hydrocarbon. For instance, when one pair of distal ring bonds is fixed at the optimal length for the square molecule and the preferred length of the remaining pair of ring bonds is computed, the energy is minimized at a square geometry.

The behavior of cyclobutadiene can be understood mathematically on the basis of a quadratic potential for small distortions from a square geometry,[7]

$$E = k(x^2 + y^2)/2 + k'xy \qquad (1)$$

where x and y are the deviations of the two sets of distal bond lengths from those at a square geometry. There are no linear terms in the potential, since b_{1g} distortion of square to rectangular cyclobutadiene involves mixing of a low-lying $^1A_{1g}$ excited state into the $^1B_{1g}$ ground state.[3,4] Consequently, the energy lowering due to this second-order Jahn–Teller effect is quadratic in the distortion. The favorability of a b_{1g} distortion in cyclobutadiene is manifested in the fact that $k' > k$, so that for $x = -y$ the energy is obviously lowered. However, if $x = 0$, the optimal value for y is also zero; and the molecule remains square.

The cyclobutadiene cation radical differs from the neutral molecule in that the energy lowering on rectangular distortion is due to a first-order Jahn–Teller effect. For a b_{1g} distortion the energy lowering is, therefore, linear in the distortion. Thus, the energy around the optimal square geometry can be expressed as

$$E = -k''|x - y| + [k(x^2 + y^2)/2] + k'xy \qquad (2)$$

This equation shows that even if $x = 0$, the optimal value of $y \neq 0$. In fact, if k' is small enough to be neglected (as seems likely since there should be no second-order Jahn–Teller effect for a b_{1g} distortion of ^2E_g), the optimal distortions of the two sets of bonds are independent and each equal in magnitude to k''/k. Therefore, unlike the neutral tetra-*tert*-butylcyclobutadiene, the radical cation should have a distinctly nonsquare geometry. Steric repulsions may lead to lengthening of the shorter set of bonds from those predicted for the parent radical cation, but no accompanying contraction of the longer set of bonds is expected.

In order to test the prediction made from eq 2, regarding the independence of the distortions along the two sets of bonds in the radical cation, we carried out geometry optimizations with one set of bonds held at 1.469 Å, the optimal bond length for the square molecule at the σ–π CI level of theory. Two minima were found, one at $y = 0.057$ Å and the other at $y = -0.555$ Å. These bond length distortions from the optimal square geometry are almost exactly the same as those found at the optimal rectangular structure. Moreover, the sum of the two corresponding energy lowerings was 0.0112 hartree, precisely the energy drop calculated for distortion of the square radical cation to the optimal rectangular geometry.

The individual differences between the energy of the square radical cation and the energies at the two minima were 0.0062 and 0.0050 hartrees, with the larger stabilization energy corresponding to bond shortening. The two numbers are unequal because the quadratic force constants around the two minima are

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[23] Krogh-Jespersen, K.; Schleyer, P. von R.; Pople, J. A.; Cremer, D. *J. Am. Chem. Soc.* **1978**, *100*, 4301.

[24] We used the analytical gradient based geometry optimization routine in Dupuis, M.; Spangler, D.; Wendolosky, J. J. GAMESS, National Resource for Computation in Chemistry. We thank Dr. Dr. Dupuis and the National Resource for Computation in Chemistry for making this program available to us.

[25] Only C_2 symmetry was imposed on the SCF wave function, but it emerged with the full D_2 molecular symmetry. However, at rectangular geometries near D_{4h}, when calculations were carried out with only C_{2h} symmetry imposed on the wave function, the MO's that were obtained had less than the full D_{2h} molecular symmetry.

[26] Irngartinger, H.; Rodewald, H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 740.

[27] Delbaere, L. R. J.; James, M. N. G.; Nakamura, N.; Masamune, S. *J. Am. Chem. Soc.* **1975**, *97*, 1973.

[28] Support for this proposal comes from unpublished molecular mechanics calculations carried out by W. D. Hounshell, and K. Mislow. They find that the energy lowering due to relief of repulsions between *tert*-butyl groups on going from a rectangular to a square geometry is almost exactly the same as the energy, calculated by ab initio theory,[1-4] required to transform the parent molecule from its rectangular equilibrium geometry to a square. We thank Professor Mislow for communicating these results to us.

different, with greater energy being required to stretch the bonds with the larger π bond order than to compress the pair with weaker π bonding.

The stabilization energy of 3.1 kcal/mol, computed for lengthening just one set of bonds in the radical cation while holding the other set fixed at the optimal length for the square geometry, is still considerably more than the stabilization energy of only 1.0 kcal/mol that is calculated for rhomboidal distortion. This finding suggests that in the radical cation derived from tetra-*tert*-butylcyclobutadiene, a rectangular distortion should still remain preferable to a rhomboidal one, although the energy difference between the two might well be smaller than in the parent radical cation.

Comparison with Cyclobutadiene

Although electron repulsion complicates carrying out *calculations* on the radical cation, electron repulsion plays a much smaller role in the *behavior* of this species than in the neutral molecule. This is due, of course, to the fact that one of the two nonbonding electrons in cyclobutadiene is absent in the radical cation. Consequently, the radical cation behaves just as one would expect from inspection of the degenerate Hückel MO's (Figure 2), with distortions from square to both rectangular and rhomboidal geometries being favorable. The calculated preference for the former over the latter can be understood from the nodal patterns in the MO's that are appropriate for describing each of the distorted structures and the fact that π interactions between nearest neighbor atoms are more important than those between atoms diagonally across the four-membered ring.

In contrast, in the ground state of the neutral molecule a rhomboidal distortion is unfavorable,[3,4] since it requires placing both nonbonding electrons in one of the π MO's that is localized to two atoms along a diagonal plane of symmetry. Minimization of electron repulsion in square cyclobutadiene actually causes only one of the nonbonding electrons to occupy each of these MO's;[11] therefore, the ground state of the square molecule is incapable of profiting from a rhomboidal distortion. Consequently, unlike the radical cation, which can pseudorotate from one rectangular minimum to another via a rhomoboidal geometry, the neutral molecule cannot avoid passing through a square transition state.

Electron repulsion in the neutral molecule is also responsible for the fact that the energy lowering, computed at the σ–π CI level, for distortion from a square to a rectangular geometry is very similar for both the neutral molecule and the radical cation. The stabilization energies are similar, despite the presence in the neutral molecule of one more electron in the e_g π orbitals that induce the distortion. Although the additional electron does result in cyclobutadiene being predicted to have a more rectangularly distorted equilibrium geometry than the radical cation,[1-4] in the neutral molecule rectangular distortion from a square increases the Coulombic repulsion energy between the pair of nonbonding π electrons.[11] This increase partially cancels the energy lowering due to the stronger π bonding (in the Hückel sense) at the rectangular equilibrium geometry of the neutral molecule.

If π bonding, which is maximized at a rectangular geometry, is disrupted by lengthening the strong π bonds or shortening the weak ones, the neutral molecule tends toward a square geometry in order to minimize the Coulomb repulsion energy between the nonbonding electrons.[7] In contrast, in the radical cation, where only one nonbonding electron is present, this effect is absent. Consequently, unlike the case in the neutral molecule, the two sets of bond lengths in the radical cation are independent of each other. This is the physical origin of the difference in behavior that is predicted by eq 1 and 2 and confirmed computationally by the results of our ab initio calculations.

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Location and Relative Orientation of Methanol Adsorbate Molecules in A, X, and Y Zeolites from Electron Spin–Echo Studies

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Abstract: Hydroxymethyl radicals have been generated by γ-radiolysis at 77 K from specifically deuterated methanols, CD_3OH and CH_3OD, adsorbed on NaA, Ca_4Na_4A, NaX, KX, NaY, and KY zeolites. These radicals have been studied by electron spin–echo spectrometry and the deuterium modulation patterns analyzed. In A zeolites, the hydroxymethyl radical is located in the α-cage above a hexagonal interior face, with the molecular radical's electric dipole oriented along the threefold axis of the hexagonal face. Since a majority of the cations are in or near the hexagonal faces this orientation is consistent with a cation charge–molecular dipole interaction controlling the adsorbate geometry. The radical interacts with three equivalent closest methanol molecules in the α-cage, with their methyl groups 0.38 nm from the α-carbon of the radical. The radical location and orientation in X and Y xeolites is similar, except that both square and hexagonal faces are involved and the three nearest interacting methanol molecules lie slightly further away.

Zeolites are hydrated aluminosilicates with a cage structure and are widely used for sorption and catalysis.[1] A variety of investigations have been conducted into the thermodynamics and kinetics of sorption of various materials on synthetic zeolites. Electron spin resonance studies[2-5] have yielded some information on interactions between adsorbed molecular radicals and zeolitic interior surfaces. However, the continuous wave methods used in most electron spin resonance experiments are not very suitable for studying the weak interactions between a paramagnetic center and adsorbate molecules or with the lattice nuclei. Even though some crystal structure information is available, relatively little

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