both terminal groups occurs within the diradical species; (iii) the majority of the reactive trajectories lead, especially at low total intramolecular energies, to formation of the optical isomer, via the half-way point EE. This result can be simply explained on the basis of the static potential energy surface; the activation energy required to reach the coplanar diradical (EE) is lower than that required to reach the orthogonal diradical (EF). No dynamical factor tends to inverse the preference for the minimum energy path over any other path. This conclusion is in good agreement with recent experimental tests of the relative rates of optical and geometrical isomerizations in optically active *trans*-cyclopropane-*1,2*-d_2 and 1-phenylcyclopropane-*2*-*d*.[23] The kinetic analysis of these reactions is consistent with a mechanism involving exclusive synchronous rotation of two methylene groups.

In connection with the experimental estimates of the relative rates of rotations and C–C cleavage in three- and four-membered rings,[24] we are presently studying the influence of heavy substituent groups on the dynamical coupling between the ring opening (or closure) and the rotations of the terminal groups.

Acknowledgment. Professor Lionel Salem's very helpful contributions to the present study are gratefully acknowledged.

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Theoretical Studies of the Protonation of Cyclobutane

Tapani Pakkanen* and J. L. Whitten

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794.
Received April 28, 1975

Abstract: The protonation of cyclobutane has been studied theoretically using ab initio methods. The protonation energy is found to be quite large, 126 kcal/mol, but is significantly lower than obtained for the protonation of cyclopropane by similar theoretical calculations. The protonation energies for edge and corner protonation of cyclobutane were found to be essentially identical.

The relative stabilities of protonated cycloalkanes have been a subject of recent experimental and theoretical studies.[1-7] These compounds have been postulated to be intermediates in acid-catalyzed reactions. The structure of protonated cyclopropane has been discussed thoroughly in several studies[1-4] but the evidence for the structure, formation, and even the existence of protonated cyclobutane is much less convincing.[5-10] In the present work, the protonation of cyclobutane is studied theoretically by ab initio SCF methods using a flexible basis set of atomic orbitals. The level of accuracy of the treatment is such as to provide a good assessment of the energy of protonation. In previous experimental work, Cacace et al.[9] have reported on the gas-phase protonation of cyclobutane using the helium tritide, He^3H^+, molecular ion which is an extremely strong acid. They interpret their results as direct evidence for the forma-

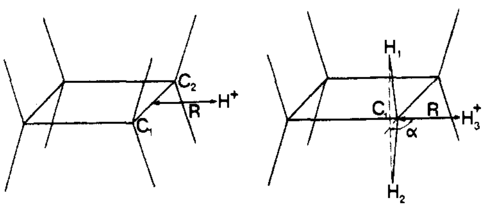

Figure 1. Geometries of edge and corner protonated cyclobutanes. The angle H$_1$-C$_1$-H$_2$ is 120° in the corner protonated cyclobutane.

Table I. The Orbital Energies and the Total Energy of Cyclobutane

	Orbital energies		
Orbital symmetry	This work, (eV)	Wright and Salem,[a] eV	Exptl[b] (photoelectron spectra), eV
$1a_{1g}$	−304.902	−304.850	
$1e_u$	−304.888	−304.849	
$1b_{2g}$	−304.873	−304.847	
$2a_{1g}$	−30.246	−29.539	
$2e_u$	−24.166	−23.678	
$2b_{2g}$	−19.748	−19.504	
$1a_{2u}$	−17.847	−17.287	−18.2
$3a_{1g}$	−16.863	−16.712	−15.9
$1e_g$	−14.581	−14.133	−13.4, −13.6
$1b_{1g}$	−13.047	−12.715	−12.5
$1b_{1u}$	−11.924	−11.624	−11.7
$3e_u$	−11.236	−11.050	−10.7, −11.3
Total energy[c]	−156.015965 au	−155.8370 au	

[a] Reference 13. [b] Reference 15. [c] 1 au = 27.2107 eV.

Table II. The Total Energy and Orbital Energies of the $7a_1$ and $6a_1$ MO's of Edge Protonated Cyclobutane as a Function of the Proton Distance R (Energies are in au and R is in Å)

R	Total energy	$7a_1$ orbital energy	$6a_1$ orbital energy
0.652	−156.1905	−0.677	−0.868
0.829	−156.2196	−0.671	−0.840
0.906	−156.2221	−0.669	−0.830
0.986	−156.2200	−0.666	−0.819
1.128	−156.2075	−0.661	−0.798
1.338	−156.1794	−0.655	−0.773

tion of protonated cyclobutane. The isomerization process of an initially protonated species, probably protonated cyclobutane, was studied also by Lias et al.[10] who found the isomerization product to be the *sec*-butyl ion. The corresponding protonation reaction in solution was attempted by Olah and Lukas.[7] They were not able to identify protonated cyclobutane in the solution of cyclobutane and the strong acids fluorosulfonic acid and antimony pentafluoride, whereas protonated cyclopropane was detected under the same conditions.

The relatively lower energy of protonation of cyclobutane compared to the protonation of cyclopropane has been also postulated by Wiberg et al.[5,8] based on a theoretical analysis of the available molecular orbitals. They also point out that kinetic studies indicate that a molecule containing the cyclopropane ring is at least 10^6 times more reactive toward electrophiles than a corresponding compound containing the cyclobutane ring.

There have not been many theoretical calculations on the protonation of cyclobutane and in all of the reported studies highly approximate methods have been employed. A perturbation theory method applied to Hückel molecular orbitals as basis functions has been used to compare different protonation sites in cyclobutane,[6] and Wiberg et al.[5] have reported CNDO calculations for edge and corner protonated cyclobutanes. The latter authors concluded that their calculations were not adequate to determine the relative energies of edge protonated cyclopropanes and cyclobutanes.

The objectives of the present study are threefold: (1) to determine the protonation energy of cyclobutane by considering both edge and corner protonated species, (2) to analyze the effects of the proton on the molecular orbitals of cyclobutane, and (3) to make a comparison of the energy of protonation of cyclobutane with previously reported studies of the protonation of cyclopropane.

Calculations

The ab initio molecular orbital calculations were carried out using standard LCAO-SCF techniques. A gaussian lobe basis of atomic Hartree-Fock quality was used for carbon and hydrogen.[11] In order to achieve additional flexibility in the representation of molecular orbitals, the atomic orbitals were decomposed into four s groups and two-p groups for carbon, i.e., the extended basis of ref 11 denoted by [10s, 5p/4, 2] for C and [5s/1] for H. Thus in this approach, considerable variation of the shape of individual atomic orbitals is permitted at the molecular SCF level, and consequently an improved description of bonding is achieved over minimal basis treatments. In the edge protonated cyclobutane an extra s-type basis function was used at the midpoint of the C-C bond to improve the description of the edge protonation site. Reference calculations without this basis function were also carried out. Molecular symmetry was used extensively to avoid the computation of equivalent integrals. The structure of cyclobutane is known to be puckered, with a dihedral angle of about 30° (see ref 12), and the barrier to inversion is ~1.4 kcal/mol. Because of this rather shallow barrier, and also the uncertainty in the exact dihedral angle, the planar geometry was chosen for all calculations. The assumed geometrical parameters of cyclobutane were taken as follows: C-C bond lengths, 1.553 Å; C-H bond lengths, 1.095 Å; and an H-C-H angle of 112°; in the calculations, 1 au = 0.529167 Å.

Results

A. Cyclobutane. The planar cyclobutane has C_{4h} symmetry and in Table I a comparison with previous ab initio calculations[13,14] shows that the present results give the same ordering of the occupied molecular orbitals. The orbital energies are somewhat lower in the present work, and the total energy is significantly lower than in previous studies due to the improved basis set. Also the orbital energies are in a good agreement with the photoelectron spectrum,[15] assuming the necessary cancellation of effects in the use of Koopmans' theorem.

B. Edge Protonated Cyclobutane. Figure 1 shows the geometry of the edge protonated cyclobutane; R is the distance of the proton from the midpoint of the C$_1$-C$_2$ bond. The energies for different distances R are presented in Table II. The optimum distance is 0.906 Å and the corresponding total energy is −156.22205 au. As mentioned in the previous section, an extra basis function was used in these calculations, and without this basis function the total energy is −156.21705 au for R = 0.906 Å. This gives a proton binding energy of 5.47 eV (126.2 kcal/mol). Table III gives a comparison of the orbital energies of cyclobutane and protonated cyclobutane. Also in Table II, the orbital energies of the $7a_1$ and the $6a_1$ orbitals are given for different values of R. The significance of these variations will be discussed subsequently.

C. Corner Protonated Cyclobutane. The optimization of all the geometrical parameters of corner protonated cyclobutane was not practical and, therefore, the geometrical variations allowed in this set of calculations were restricted to be of the same type as in the edge protonated case. Fig-

Table III. A Comparison of the Orbital Energies of Cyclobutane and Edge Protonated Cyclobutane (Energies Are in au and R is 0.906 Å)

Cyclobutane		Protonated cyclobutane	
Orbital	Orbital energy	Orbital	Orbital energy
$1a_{1g}$	−11.2052	$1a_1$	−11.4913
		$1b_2$	−11.4908
$1e_u$	−11.2047	$2a_1$	−11.4438
$1b_{2g}$	−11.2042	$2b_2$	−11.4433
$2a_{1g}$	−1.1115	$3a_1$	−1.4328
$2e_u$	−0.8881	$4a_1$	−1.2114
		$3b_2$	−1.1411
$2b_{2g}$	−0.7257	$4b_2$	−0.9775
$1a_{2u}$	−0.6559	$1b_1$	−0.9193
$3a_{1g}$	−0.6197	$5a_1$	−0.8825
$1e_g$	−0.5359	$1a_2$	−0.7913
		$2b_1$	−0.7802
$1b_{1g}$	−0.4795	$6a_1$	−0.8295
$1b_{1u}$	−0.4382	$2a_2$	−0.6752
$3e_u$	−0.4129	$5b_2$	−0.6697
		$7a_1$	−0.6685

ure 1 shows the allowed variations in R and α where R is the distance of H^+ from C_1, and α is the angle H_3–C_1–H_{12}, H_{12} denoting a point on the bisector of H_1–C_1–H_2. A minimum on the two-dimensional potential-energy surface was found for $R = 1.095$ Å and $\alpha = 80°$. The corresponding total energy is −156.21761 au which is essentially identical with the minimum energy in the edge protonated case without the extra basis function at the midpoint of C_1–C_2.

D. Mulliken Population Analysis. Figure 2 shows the results of a Mulliken population analysis for cyclobutane, and for the edge and corner protonated cyclobutanes.

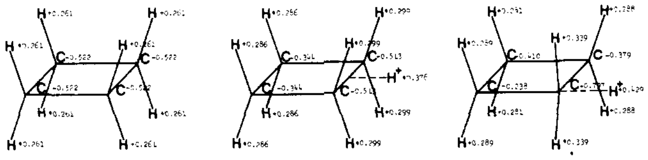

Figure 2. Mulliken population analysis for cyclobutane, and for edge and corner protonated cyclobutanes.

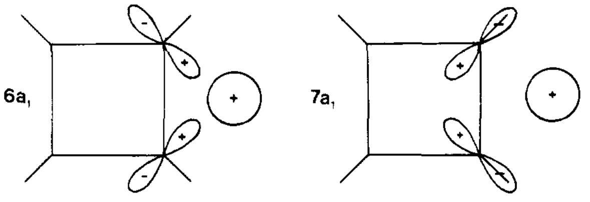

Figure 3. $7a_1$ and $6a_1$ orbitals of edge protonated cyclobutane.

Table IV. Energy Changes for the Reactions $C_3H_7^+ \rightarrow C_3H_6 + H^+$ and $C_4H_9^+ \rightarrow C_4H_8 + H^+$

Protonated cycloalkane	Protonation site	Protonation energy, kcal/mol	Ref
$C_3H_7^+$	edge	176.9	*a*
	edge	155.0	*b*
	corner	186.6	*a*
$C_4^+H_9^+$	edge	126.2 (129.3)[d]	*c*
	corner	126.5	*c*

[a] Reference 2. [b] Reference 1. [c] This work. [d] s-Type basis function in the midpoint of C–C bond.

Discussion

The calculations predict that the protonation of cyclobutane is an energetically favorable process, 126 kcal/mol exothermic. The protonation energies for cyclopropane and cyclobutane are presented in Table IV. If the results for cyclobutane are to be compared with the edge protonation energy of cyclopropane, the comparison should likely be made with the results of Petke and Whitten,[1] since the atomic basis sets are of the same quality and the degree of the optimization of the geometry is similar to that in this work. However, the additional flexibility of the basis used for protonated cyclobutane, discussed in the Calculations section, means that the present study is at a superior level of accuracy than the previous work on protonated cyclopropane. Thus, for purposes of comparison, the protonation energy of cyclopropane should probably be taken at a somewhat higher value than the 155 kcal/mol value of Table IV. In any case, it is clear from the results of Table III that the proton binding energy is quite large for protonated cyclobutane (126 kcal/mol), but that the value is significantly smaller than that for protonated cyclopropane, particularly since the latter value probably should be increased. The possible reasons for the differences have been discussed previously by Wiberg[5] and Hoffmann.[16] This work supports the postulate that the highest filled MO in cyclobutane is not able to bind the proton very effectively on edge protonation. The energies of the highest filled, $7a_1$, orbital and the best proton binding orbital, $6a_1$, as a function of the proton distance R are presented in Table II. The stabilization of the $7a_1$ orbital is not significantly greater than the stabilization of the cyclobutane MO's in general on protonation. (See Table III.) The $6a_1$ MO, on the other hand, is favorable to bind the proton, and it is stabilized strongly when the proton distance R is decreased. Figure 3 shows the general features of the $7a_1$ and $6a_1$ orbitals. In the protonation of cyclopropane the best binding orbital is the highest, and this is probably the most significant reason why cyclobutane is less easily protonated. On the question of the relative stability energetically of corner or edge protonated cyclobutane, the protonation energy is found to be essentially identical in both cases for the same basis set and the same degree of optimization of geometry. This is not very surprising if we compare the equilibrium geometries of the two species. In the edge protonated cyclobutane the distance of the proton from the nearest carbon is 1.19 Å, very close to the 1.095 Å in the corner protonated case. The angles H_3–C_1–H_{12} are 80 and 85°, respectively, and the CH_3 groups have approximately the same internal geometry in both cases.

Further geometrical variations opening the ring structure of $C_4H_9^+$ would be very informative; see, for example, such studies of the potential surface of $C_3H_7^+$, ref 2 and 3. However, it should be noted that a reliable assessment of the relative stabilities of the different cationic structures is not necessarily achieved by small basis calculations.

Acknowledgment. The authors wish to acknowledge helpful conversations with Dr. Jawed Jafri. One of us (T.P.) was supported by an ASLA-Fulbright grant and by the Neste OY Foundation, which is gratefully acknowledged. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Services and computer time made available by the State University of New York at Stony Brook Computing Center have been invaluable in this study.

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Molecular Shapes and the Pauli Force. An Outdated Fiction

James L. Bills* and Richard L. Snow

Contribution from the Department of Chemistry, Brigham Young University, Provo, Utah 84602. *Received June 5, 1974*

Abstract: Molecular-orbital calculations neglecting interelectronic Coulomb repulsions in the water molecule show that its shape is not determined by the Pauli exclusion principle. The water molecule is also used to test a recent definition of the Pauli force as the change in interatomic Coulomb force that results from orbital orthogonalization. Theoretical arguments are given against the dependence of the molecular shape on this electrostatic Pauli force, and the possibility of empirical correlation of the two is ruled out by calculation of discrepant indices of the Pauli force. The insufficiency of the Pauli principle to explain molecular shapes is further demonstrated by showing that Slater determinations of atomic orbitals are incapable of discriminating between observed and unobserved molecular shapes. The Pauli force appears to be a useless and even misleading fiction.

The "Pauli force" is a fictitious force invented to help a person to visualize the effect of the antisymmetry requirement of the Pauli exclusion principle on the spatial distribution of electrons.[1] In support of the fiction that the Pauli force keeps electrons of like spin separated in space, the wave function does vanish whenever two such electrons are assigned the same coordinates. Recent evidence, however, indicates that an electron's exclusive domain or "Fermi hole" is quite local[2] and generally does not have the expected effect either on the average interelectronic distance[3] or on the energy of repulsion[4] when states of different multiplicity are compared. The familiar explanation[1,5] of Hund's rule has been shown to be incorrect,[4] leaving no doubt that the concept of the Pauli force can be completely misleading. The time has come to investigate the validity of other applications of the Pauli force, and to reevaluate its usefulness as a fiction.

In this paper, we show that the Pauli force does not provide a valid explanation for molecular shapes, nor does the Pauli principle itself provide one. Using the water molecule as our test case, we first consider the Pauli force in the absence of the Coulomb force, and we then investigate the Pauli force defined as part of the Coulomb force. We conclude with some observations on Slater determinants of atomic orbitals.

The Pauli Force without the Coulomb Force. As justification for this section, we point out that the currently popular valence-shell electron-pair repulsion theory (VSEPR) assumes the existence of a Pauli force that has its own force law,[6a] that is more important than the Coulomb force in determining molecular shapes,[6b] and that can be used to deduce molecular shapes even when the Coulomb force is neglected.[6c] Other authors have also drawn a distinction between the Pauli force and the Coulomb force.[7] We have found that when the Coulomb force between electrons is neglected, molecular-orbital theory predicts a linear structure for the water molecule. Aside from the neglect of interelectronic Coulomb repulsions, we followed the procedure of Roothaan,[8] where each molecular orbital (MO) is written as a linear combination of atomic orbitals (LCAO). Our AO's were hydrogenic orbitals, with $Z = 8$ for oxygen. The O–H bond length was fixed at 1.8111 au[9] (1 au = 0.05292 nm), and calculations were made for bond angles of 90, 135, and 180°. The total energies obtained at these angles are −130.070, −130.161, and −130.184 hartrees, respectively. Of course, the MO's actually pertain to the H_2O^{9+} ion rather than H_2O, and will not be given here.[10]

The incorrect prediction of a linear structure for water is proof that molecular shapes generally cannot be explained without the Coulomb force between electrons, as has been suggested.[6c,7a] Furthermore, the differences in the total energies at the three angles were determined almost entirely by the differences in the Coulomb repulsion between the hydrogen nuclei.[11] No preference for any bond angle was attributable to the Pauli force or even to the Pauli principle, which was equally satisfied by the molecular wave functions at all three angles.

Since the Pauli force is completely ineffective in the absence of the Coulomb force, the only possible way for the Pauli principle to affect molecular shapes would be through the Coulomb force. This possibility is considered in the next section.

The Pauli Force as Part of the Coulomb Force. As shown by Salem,[12] the change in electron density, $\Delta\rho_{ab}$, that occurs when two filled nonorthogonal orbitals, ϕ_a and ϕ_b, are orthogonalized is

$$\Delta\rho_{ab} = -4S_{ab}\phi_a\phi_b + 2S_{ab}^2(\phi_a^2 + \phi_b^2) \qquad (1)$$

where S_{ab} is the overlap integral between ϕ_a and ϕ_b. Since the orthogonalized orbitals satisfy the Pauli principle, Bader and Preston[13] interpreted $\Delta\rho$ as the effect of the Pauli principle on the electron density. They defined "Pauli repulsions" as the changes in the Coulomb repulsions on the nuclei brought about by $\Delta\rho$. They concluded that the Pauli