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Supplementary Material Available: Listings of atomic coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors (11 pages). Ordering information is given on any current masthead page.

Coupling of Internal Motions in Bicyclobutane Radical Cation: The Effect of a Positive Charge on a Radical Center[1]

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Although bicyclobutane has been known for almost 30 years,[2] reports regarding its radical cation have appeared only in the last few years.[3] Recently, we have found that bromination of bicyclobutane derivatives occurs by an electron-transfer mechanism involving the radical cation of bicyclobutane as a reaction intermediate.[4] Consistency with the stereochemistry observed for the reaction requires that the postulated intermediate be stable in a highly puckered geometry. In order to test this assumption, an ab initio UHF/SCF study at the 3-21G level[5] was conducted in which the angle α was varied between 115° and 180° (see Figure 1) with full geometrical optimization at each α value. The results obtained confirmed the stability of the radical cation in its puckered form with $\alpha = 122°$.[4] In addition, interesting and unexpected couplings among the various geometrical parameters of the radical cation accompanying the variation in α were revealed. These latter results are given in Table I.

From Figures 1 and 2 it can be seen that other bond lengths and angles of the molecular geometry change significantly as α increases from 140° ($r = 1.85$ Å) to 160° ($r = 2.1$ Å). A particularly dramatic change is observed in the lengths of the side bonds r_1 and r_2 which become unequal. This result is due to a change in electronic structure from a symmetric (C_{2v}) delocalized charge distribution to a charge localized structure having C_s symmetry.[6] Localization of the positive charge on $C_{(1)}$ induces the shortening of r_1. The lengthening of r_2 results from a decrease of the bonding charge density in r_2 due to the hyperconjugative interaction between the σ bond orbital associated with r_2 and the vacant orbital on $C_{(1)}$.

Table I. Selected Geometrical Parameters for the Radical Cation as a Function of α[a]

fixed	optimized			
α (deg)	β (deg)	γ (deg)	r_1 (Å)	r_2 (Å)
115	159.7	159.7	1.518	1.518
120	157.2	157.2	1.515	1.515
122.68	156.0	156.0	1.515	1.515
125	154.9	154.9	1.515	1.515
130	152.8	152.8	1.514	1.514
140	149.2	149.2	1.515	1.515
150	151.2	146.6	1.491	1.551
153	160.6	148.8	1.489	1.561
157.5	174.9	196.7	1.497	1.548
160	175.9	196.7	1.496	1.547
170	178.3	192.1	1.496	1.541
179.9	180.0	180.7	1.496	1.538

[a] See Figure 1 for the assignment of α, β, γ, r_1, and r_2.

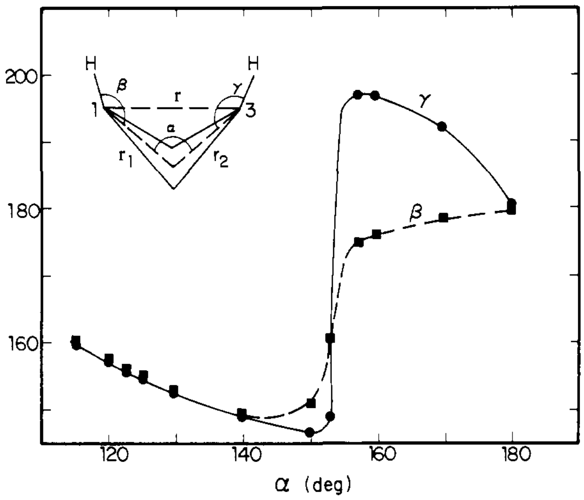


Figure 1. Optimum values of the angles β and γ for fixed values of the angle α.

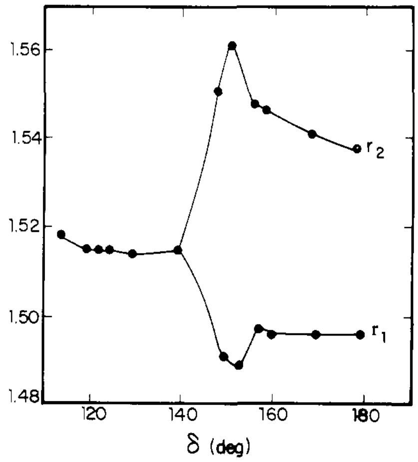
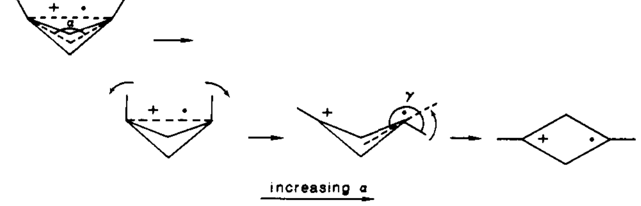


Figure 2. Optimum values of the side C-C bond lengths r_1 and r_2 for fixed values of the angle α.

Scheme I



With increasing α the bridgehead substituent at $C_{(1)}$ moves first inward (decreasing β) and then, starting at α around 145°, tilts in the reverse direction. This unusual flip motion has been previously observed in neutral bicyclobutane.[7] Its origin apparently

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(1) (a) This is part 14 in the series Cyclobutane-Bicyclobutane System. For part 13 see ref 4.

(2) For a relevant review of the chemistry of bicyclobutane, see: Hoz, S. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Patai, S., series, Ed; Wiley, New York, 1987; Chapter 19.

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(6) (a) At the α value points which showed C_{2v} symmetry for the molecular wave function, in moving from point to point induced distortions to lower symmetry of the molecular skeleton disappeared as the system relaxed back to C_{2v} symmetry in the geometry optimization. (b) See, also: Liebman, J. F.; Greenberg, A. In *The Chemistry of The Cyclopropyl Group*; Rappoport, Z., Ed.; Patai, S., series Ed.; Wiley, New York, 1987. (c) Relaxation of the symmetry of the charge localized structure to C_1 shows the bicyclic form of the cation to be a local minimum. (d) Geometry optimization at the UMP2 level also gives a change in the electronic structure from C_{2v} to C_s but at an α value that is larger by ~15° than in the UHF calculations.

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stems *from* a balance between an attempt to maximize bonding between the two bridgehead carbons and the tendency toward a planar CH_3^+ geometry. An inward tilt of the bridgehead hydrogen improves the orbital alignment which promotes bonding at smaller α as the dominant effect. However, at larger bridgehead carbon separations, the energy balance will change in favor of a planar geometric configuration surrounding $C_{(1)}$. The increase in both α and β is bound to decrease the hyperconjugative interaction that lengthens r_2, and, therefore, eventually, with increasing α, r_2 begins to shorten.

Much more surprising, however, is the affect of α on the motion of the substituent at the bridgehead where the radical center develops ($C_{(2)}$). Following the variation in α as it increases, this angle (γ) first decreases and then, at around $\alpha = 153°$ ($r = 2.0$ Å), rises steeply *overshooting the planar geometry* ($\gamma = 180°$) by ca. 16.7°. The value of γ then goes down again approaching planarity from the opposite direction (this process is described in Scheme I). The maximum overshoot angle ($\gamma = 197°$) is obtained at α around 160°. With use of the 3-21G optimized geometry for the radical cation at $\alpha = 160°$ but in the higher level 6-31G* basis, the hydrogen atom tilt inward was followed from $\gamma = 197°$ to $\gamma = 165°$ in several steps. The total energy was found to rise monotonically by 2.5 kcal/mol, showing the basis set independence of the second oscillation.

To the best of our knowledge, a double oscillation such as that exhibited by the second bridgehead hydrogen has never been reported before. The first oscillation of the latter hydrogen is similar to that calculated for the hydrogen on $C_{(1)}$ and stems probably from the same origin. The cause of the second oscillation, however, is less clear. We note that the "overshoot" in γ takes place when the covalent interaction across the ring has been practically nullified, and the localization of the positive charge on $C_{(1)}$ has, by and large, been completed. On this basis one could suspect that the pyramidalization results from an interaction between the positive charge and the radical center. Such a pyramidalization may be due to polarization of the SOMO toward the positive charge and/or to the repulsion between the latter and the partly positively charged hydrogen atom.

In order to examine the hypothesis that this overshoot effect is caused by the neighboring positive charge, a model system was studied. It consisted of a unit positive charge located 1.5 Å away from the carbon atom along the symmetry axis of a planar methyl radical. Optimization of the methyl fragment at the 3-21G level[5] (UHF) showed indeed a symmetric pyramidalization of 6.85° (which in terms of the angle γ in our case is equivalent to 200.4°). A symmetric pyramidalization of 5.6° (196.65° in terms of γ) was obtained by using the 6-31G* basis set.[8] Finally, the system of $Me^\bullet$ with Na^+ replacing the positive charge was fully geometry optimized by using the 6-31G* basis set[8] for the Me fragment and CEP-31G[9] basis and core potential for Na (UHF). The equilibrium geometry has a C–Na distance of 2.73 Å and a symmetric pyramidalization angle of 7.8°.

The aforementioned ab initio predicted effect of a positive charge on the geometry of a radical center is amenable to experimental verification. The best probe would probably be the determination of the ESR coupling constants of the substituents around the radical center in a caged or folded structure in which the radical center is located close to a positively charged group such as the quaternary ammonio substituent embedded in the molecular framework.

Acknowledgment. We gratefully acknowledge helpful discussions with Prof. M. Sprecher of this department.

Registry No. Bicyclobutane radical cation, 85915-57-7; methyl radical, 2229-07-4; sodium ion, 17341-25-2.

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Ethylene Formation in the Reduction of 1,4-Dihaloalkanes with a Nickel(I) Macrocycle

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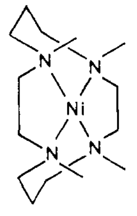
The nickel tetraaza macrocycle[1-5] Ni(tmc)$^+$ reacts with 1,4-dihaloalkanes (halide = Br, I) to produce ethylene, eq 1. No

$$\text{X}\text{–}(\text{CH}_2)_4\text{–X} + 2\text{Ni(tmc)}^+ \rightarrow 2\text{XNi(tmc)}^+ + 2\text{C}_2\text{H}_4 \quad (1)$$

cyclobutane or butenes were observed by VPC under any conditions, although suitable controls were performed to show that they would have survived the reaction conditions. 1-Bromobutane and minor amounts of *n*-butane (2–10%) result only when a deficient quantity of Ni(tmc)$^+$ is used. With excess Ni(tmc)$^+$, however, both byproducts are largely eliminated, and ethylene is formed in >90% yield.



R,*S*,*R*,*S*-[Ni(tmc)$^+$]

The reactions proceed by way of an organometallic intermediate, which is inferred to be (tmc)Ni$(CH_2)_3CH_2X^+$, because it hydrolyzes[6] to the 1-halobutane upon standing or when H_3O^+ is added. The unimolecular rate constants for hydrolysis at pH 12 are 1.3×10^{-2} and 2.7×10^{-2} s^{-1}, for X = Br and I, respectively. These values lie in the same narrow range spanned by values for the hydrolysis of other RNi(tmc)$^+$ complexes,[6] $(0.8\text{–}2.7) \times 10^{-2}$ s^{-1}. The organometallic complex can be detected spectrophotometrically (λ_{max} 405 nm, ϵ 2×10^3 M^{-1} cm^{-1}) under suitable reaction conditions. It resembles known organonickel complexes spectrophotometrically and chemically.[3,4] With excess alkyl halide the organonickel complex yields 1-bromobutane; this in turn gives minor amounts of *n*-butane from the *n*-butylnickel complex formed from it. Addition of Ni(tmc)$^+$ to this organometallic complex causes its "immediate" decomposition, accompanied by ethylene formation, eq 2. This reaction is catalytic, requiring but a trace of excess Ni(tmc)$^+$.

$$(\text{tmc})\text{Ni}(\text{CH}_2)_3\text{CH}_2\text{X}^+ \xrightarrow{\text{Ni(tmc)}^+} \text{XNi(tmc)}^+ + 2\text{C}_2\text{H}_4 \quad (2)$$
$$(\text{X} = \text{Br, I})$$

The methyl-substituted 1,4-dibromobutane $BrCH(CH_3)(CH_2)_2CH_2Br$ yields equal amounts of the analogous alkenes, ethylene and propene; no methylcyclobutane is observed. Some pentane and 1-pentene are formed from the 1-pentyl radical. Other 1,4-disubstituted compounds $Br(CH_2)_4Y$ (Y = Cl, OH, OTs) do not yield ethylene but yield organonickel complexes that hydrolyze exclusively to $CH_3(CH_2)_3Y$ (Table I). The alkene dihalide 1,4-dibromo-but-2-ene gives only 1,3-butadiene, without a detectable organonickel intermediate. The reactions shown in Scheme I are consistent with these observations.

Ethylene formation by reduction of 1,4-dihaloalkanes is rare, the usual products of single electron transfer being butane (e.g., from reaction of Cr^{2+}[7] and $Co(CN)_5^{3-}$[8]). Stable dimetallic

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(1) The complex depicted is 1*R*,4*S*,8*R*,11*S*-(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(I), which we abbreviate as *R*,*S*,*R*,*S*-[Ni(tmc)$^+$] or, when it is not confusing, simple as Ni(tmc)$^+$. Convenient electrochemical, photochemical, and chemical methods have been reported[2-4] for the preparation of the highly air-sensitive solutions of the nickel(I) reagent from the nickel(II) salt, which is very stable and readily prepared.[5]

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