stannane, **5**.[5] Thus, the distance of 3.367 Å falls well outside this new range which would appear to support significant singlet diradical character for the structure of **3** (i.e. **3b**), at least at 25 °C. The tin–carbon bond lengths are in the range of 2.16 (1)–2.22 (1) Å and the bond angles of the pentastanna[1.1.1]propellane framework follow from the geometry of this structure and the observed tin–tin bond lengths mentioned above (Figure 2).

In conclusion, the direct manner in which **3** can be prepared and isolated, together with its relatively high stability and the view provided by its molecular structure, will aid in future studies directed toward extending our knowledge concerning bonding within the Group IVB elements. Both experimental and theoretical investigations of the electronic structure and chemical reactivity of pentastanna[1.1.1]propellane derivatives are currently in progress and will be reported in due course.

Acknowledgment. We thank Dr. Cynthia Day of Crystalytics Co. for the structural analysis of **3** and **5** and the Office of Naval Research for financial support. The high-resolution mass spectrum of **3** was provided by Dr. Catherine Costello of the facility supported by the National Institutes of Health (Grant R-R-00317; principal investigator, Professor K. Biemann), from the Division of Research Resources.

Supplementary Material Available: Detailed information concerning the isolation and the spectroscopic and crystallographic analysis of **3**, including listings of atomic coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors and an ORTEP representation of **3** and **5** (24 pages). Ordering information is given on any current masthead page.

Structure of the Bicyclo[1.1.0]butane Radical Cation: An ESR Study

Fabian Gerson,* Xue-Zhi Qin,[†] and Caspar Ess

Institut für Physikalische Chemie
Universität Basel, Klingelbergstrasse 80
CH-4056 Basel, Switzerland

Else Kloster-Jensen

Department of Chemistry, University of Oslo
Blindern, Oslo 3, Norway

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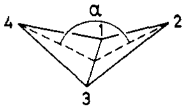
Removal of an electron from bicyclo[1.1.0]butane (**1**) affects mainly the transannular C(1)–C(3) bond,[1] so that in the radical cation $\mathbf{1}^{\bullet+}$ thus formed this bond is essentially due to one electron. The lengthening of the interatomic distance between the two bridgehead carbon atoms and the concomitant flattening of the four-membered ring upon ionization suggest that the geometry of $\mathbf{1}^{\bullet+}$ should be intermediate between the buckled **1** (flap angle α = 121.7°)[2] and the planar cyclobutane-1,3-diyl ($\mathbf{2}^{\bullet\bullet}$) ($\alpha$ = 180°).[3] Accordingly, the singly occupied orbital of $\mathbf{1}^{\bullet+}$ should evolve from the HOMO of **1** toward that of $\mathbf{2}^{\bullet\bullet}$.



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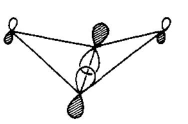
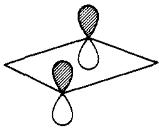


HOMO of **1**



HOMO of $\mathbf{2}^{\bullet\bullet}$

Radical cations of **1** and its derivatives have been the subject of several theoretical and experimental studies.[5] However, the hyperfine data for $\mathbf{1}^{\bullet+}$ are still unknown, although ESR spectroscopy is the most appropriate method to determine the structure of this radical cation. γ-Irradiation of **1**[6] in a $CFCl_3$ matrix at 77 K (^{60}Co source) generates $\mathbf{1}^{\bullet+}$, which, at 160 K, gives rise to the spectrum shown at the top of Figure 1. This spectrum differs dramatically from that of the cyclobutene radical cation,[7] to which **1** may rearrange upon electron removal. The well-defined hyperfine pattern of $\mathbf{1}^{\bullet+}$ consists of a two-proton triplet spaced by 7.71 ± 0.05 mT, each component of the triplet being further split by 1.14 ± 0.05 mT into a four-proton quintet.

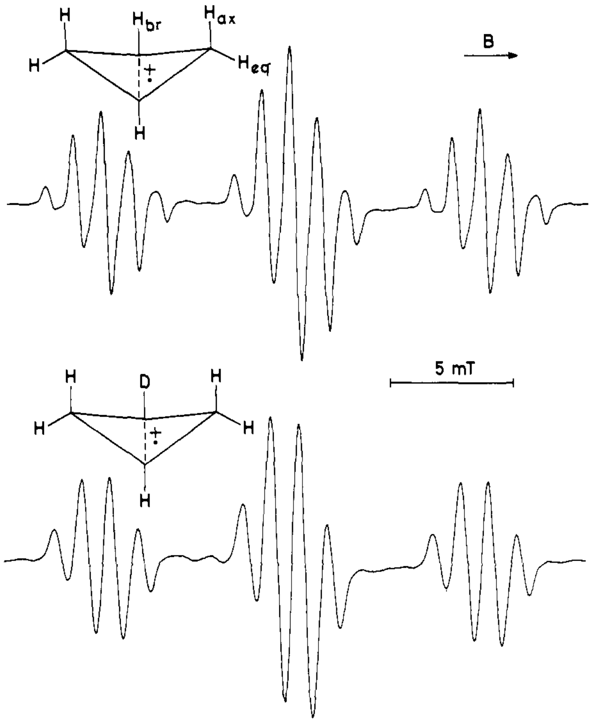


Figure 1. ESR spectra of $\mathbf{1}^{\bullet+}$ (top) and $\mathbf{1\text{-}d}^{\bullet+}$ (bottom) in a $CFCl_3$ matrix at 160 K (g = 2.0030 ± 0.0002).

An unequivocal assignment of the coupling constants to sets of equivalent protons, and hence the crucial information about the structure of $\mathbf{1}^{\bullet+}$, has been provided by an ESR study of the radical cation $\mathbf{1\text{-}d}^{\bullet+}$ generated from 1-deuteriobicyclo[1.1.0]butane (**1-d**) under the same conditions as $\mathbf{1}^{\bullet+}$ from **1**. The labeled compound **1-d** was synthesized by lithiation of **1** at a bridgehead carbon atom with *n*-PrLi, followed by reaction of the Li derivative with D_2O. In the ESR spectrum of $\mathbf{1\text{-}d}^{\bullet+}$ (Figure 1, bottom), the four-proton quintet is replaced by a three-proton quartet, as expected for the substitution of one bridgehead proton having a coupling constant of 1.14 mT by one deuteron. This finding requires the assignment of 1.14 mT to the two bridgehead protons (H_{br}) as well as to the two equatorial methylene protons (H_{eq}), while 7.71 mT represents the coupling constant of their two axial counterparts (H_{ax}). The apparent equality of the coupling constants observed for H_{br} and H_{eq} is presumably an artifact of a limited spectral resolution; even a difference as large as 0.2 mT would be obscured by the width of the hyperfine components. Also, as will be clarified by the arguments presented below, the equality or near-equality in question applies only to the absolute values of the coupling constants and not to their signs.

The strongly differing values of $a(H_{eq})$ and $a(H_{ax})$ point to a puckered geometry of $\mathbf{1}^{\bullet+}$. As no interchange between these coupling constants is observed at 160 K, the energy barrier to ring

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[†] Present address: Chemistry Division, Argonne National Laboratory, Argonne, IL 60439.

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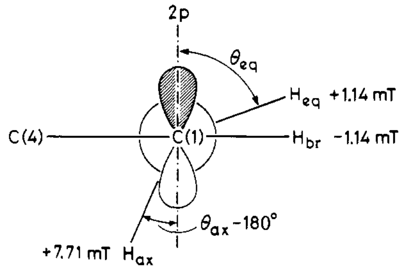
inversion through a planar geometry should be at least 12 kJ mol^{-1} when a relationship between such a barrier and the coalescence temperature is considered.[8] Moreover, the hyperfine data for $\mathbf{1}^{\bullet+}$ are consistent with the unpaired electron residing mainly in the AOs of the two equivalent bridgehead carbon atoms C(1) and C(3). These AOs must have a predominantly p character, because a spin population of 0.5 in each of them can be related to $a(H_{br})$, $a(H_{eq})$, and $a(H_{ax})$ by eq 1 and 2, where a methylene proton H_m

$$a(H_{br}) = 0.5Q \qquad (1)$$

$$a(H_m) = B(0.5^{1/2} + 0.5^{1/2})^2 \cos^2 \theta_m = 2B \cos^2 \theta_m \qquad (2)$$

stands for either H_{eq} or H_{ax}. The parameter Q in the well-known McConnell[9] equation (1) has a negative value ranging from −2.2 to −3.0 mT,[10] and thus a *negative* sign is also required for $a(H_{br}) = 1.14$ mT with $Q = -2.28$ mT. Equation 2 was first proposed by Whiffen[11] for methylene protons like H_{eq} and H_{ax} that are linked to sp^3-hybridized carbon atoms bridging *two* π centers. The parameter B is positive with a value of +4.0 to +4.8 mT appropriate for paramagnetic species of the same structural type as $\mathbf{1}^{\bullet+}$.[4,12] Therefore, the coupling constants $a(H_{eq}) = 1.14$ mT and $a(H_{ax}) = 7.71$ mT must also have a *positive* sign. The dihedral angles θ_m between the C(2)–H_m or C(4)–H_m bonds and the 2p axes at C(1) or C(3) in $\mathbf{1}^{\bullet+}$[13] cannot comply with the condition $\theta_{ax} - \theta_{eq} = 120°$, usually applied to unstrained molecules, because this difference is 211.1° − 66.1° = 145.0° in **1** (derived from the microwave data)[2] and it is 153.4° − 26.6° = 126.8° in the planar $\mathbf{2}^{\bullet\bullet}$ (calculated by a UHF-MNDO geometry optimization).[14] Assuming an intermediate value of 135 ± 5° for $\mathbf{1}^{\bullet+}$ and setting the experimental coupling constants $a(H_{ax})$ and $a(H_{eq})$ in eq 2, one obtains $\theta_{ax} = 204.5 \pm 6°$ and $\theta_{eq} = 69.5 \pm 1°$, along with $B = 4.65 \pm 0.5$ mT.

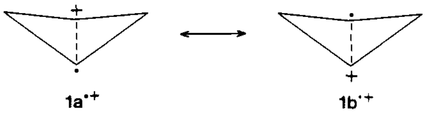


When the geometry of $\mathbf{1}^{\bullet+}$ is MNDO optimized, keeping θ_{ax} and θ_{eq} at these values, the flap angle α and the C(1)–C(3) distance come out as 132.2 ± 2.5° and 178.6 ± 3 pm. The coupling constants calculated by INDO[15] for this geometry are $a(H_{br}) = -1.20 \pm 0.01$, $a(H_{eq}) = +1.83 \pm 0.20$, and $a(H_{ax}) = +7.80 \pm 0.25$ mT, in good agreement with experiment.

Two final remarks are in order.

(i) While the C(1)–C(3) distance in $\mathbf{1}^{\bullet+}$ (178.6 pm) lies midway between those of **1** (149.7 pm)[2] and $\mathbf{2}^{\bullet\bullet}$ (UHF–MNDO, this work: 204 pm; ab initio, ref 4: 210 pm), the angles θ_{ax}, θ_{eq}, and α in $\mathbf{1}^{\bullet+}$ (204.5, 69.5, and 132.2°) are much closer to the corresponding values in **1** (211.1, 66.1, and 121.7°) than to those in $\mathbf{2}^{\bullet\bullet}$ (153.4, 26.6, and 180°).

(ii) The reasonable fit of $a(H_{eq})$ and $a(H_{ax})$ to eq 2, which requires *twice* the value B as the proportionality factor, is not compatible with a fast interconversion between charge- and spin-localized structures $\mathbf{1a}^{\bullet+}$ and $\mathbf{1b}^{\bullet+}$.[5] These structures should thus represent mesomeric formulas of $\mathbf{1}^{\bullet+}$.


$\mathbf{1a}^{\bullet+}$ $\mathbf{1b}^{\bullet+}$

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Application of an Intramolecular Tropone–Alkene Photocyclization to the Total Synthesis of (±)-Dactylol

Ken S. Feldman,* Ming-Jung Wu, and David P. Rotella

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Received April 14, 1989

Intramolecular tropone–alkene [$6\pi + 2\pi$] photocycloaddition[1,2] (eq 1) represents an efficient complement to classical acyclic closure,[3] fragmentation,[4] or ring expansion[5] strategies for the construction of the bicyclo[6.3.0]undecane skeleton characteristic of several terpenoid natural products. An exemplary member of this class of compounds is dactylol (**3**), a marine sesquiterpene isolated from *Aplysia dactylomela*,[6] which features three contiguous stereogenic centers embedded with the *trans*-bicyclo-

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