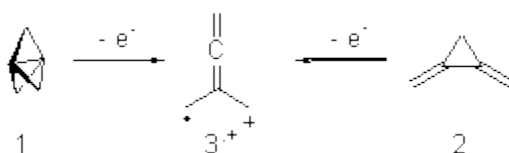


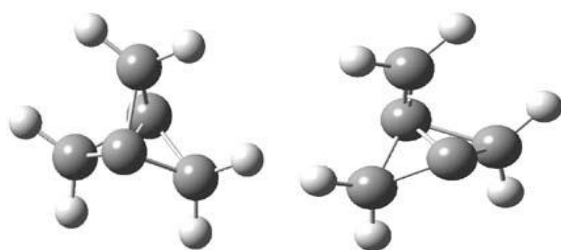
STRUCTURE OF THE PROPELLANE RADICAL CATION

Propellane **1**, whose bridgehead-bridgehead bond has a HOMO that is largely outside of the bridgehead-bridgehead region. Thus, loss of an electron to form the radical cation **1**^{•+} seems unlikely to lead to any significant geometrical change. However, the ESR of the radical cation of propellane shows two types of hydrogens, one type of four hydrogens and a second type of two hydrogens. This is incompatible with a D_{3h} structure similar to that of **1**. Furthermore, loss of an electron from dimethylenecyclopropane **2** leads to a species whose ESR is nearly identical to that of the radical cation of propellane. Analysis of the ESR suggests that the radical actually produced is **3**^{•+}.



CCSD(T)/cc-pVTZ//B3LYP/6-31G* computations were performed to try to discern a mechanism for this rearrangement. The D_{3h} structure of **1**^{•+} is a local energy minimum with most computational methods, though not with B3LYP, where it is a TS connecting mirror image C_2 structures. Breaking symmetry to C_2 leads to a TS (**TS1**) for cleaving one of the C-C_{bridgehead} bonds. This TS is

only $1.15 \text{ kcal mol}^{-1}$ above 1^+ , and leads to 4^+ , $7.38 \text{ kcal mol}^{-1}$ below 1^+ . Cleavage of a second C-C_{bridgehead} bond passes through **TS2**, with a barrier from 4^+ of only $2.89 \text{ kcal mol}^{-1}$. This leads to 2^+ . Lastly, cleavage of a third C-C_{bridgehead} bond through **TS3**, with a barrier of only $2.09 \text{ kcal mol}^{-1}$ above 2^+ , leads to 3^+ , overall $30.4 \text{ kcal mol}^{-1}$ exothermic from 1^+ . The structures of these critical points are shown in Figure 1. Quite a neat little pathway – three sequential bond ruptures without ever cleaving what was the weakest bond in the original compound (the bridgehead-bridgehead bond)!

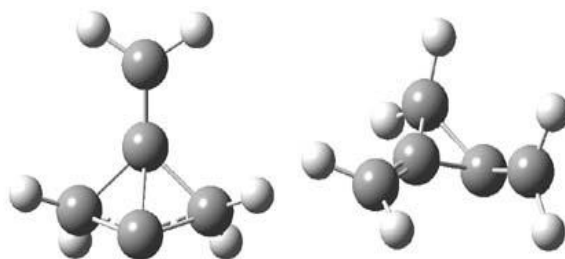


1⁺

0.0

TS1

+1.15

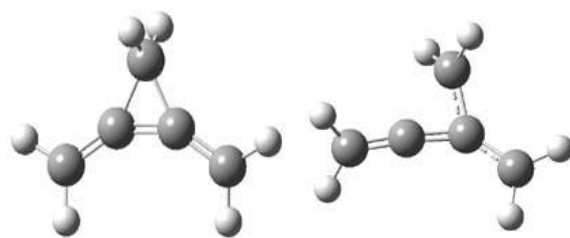


4⁺

-7.38

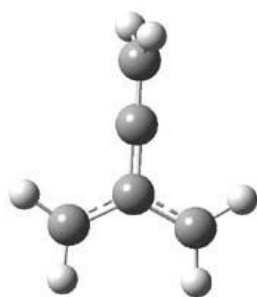
TS2

-4.49



2⁺
-24.54

TS3
-22.45



3⁺
-30.41

Table 1. B3LYP/6-31G* optimized critical points on the pathway of **1⁺** to **3⁺**.
Relative energies in kcal mol⁻¹

The cool part of this is why the barrier is so small leading out of **1⁺** – vibronic coupling via C_s distortion of **1⁺** with its first excited state leads to an energy lowering of this pathway. This sort of vibronic coupling had in fact been implicated by Heilbronner and Wiberg³ in arguing the photoelectron spectrum of **1**.

Source: <http://comporgchem.com/blog/?p=1484>