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The "Bond-Stretched Invertomer" of Hexafluorocyclopropane—a New Type of Reactive Intermediate**

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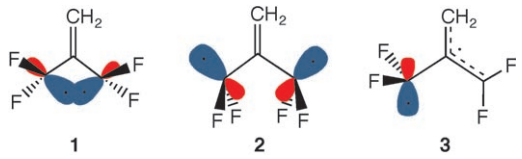
Dedicated to Professor Rolf Gleiter on the occasion of his 70th birthday

During an exploration of the potential-energy surface (PES) for the rearrangement of 2,2,3,3-tetrafluoromethylenecyclopropane (**1**),[1] we discovered a local minimum **2**, which may be regarded as a bond-stretch isomer of **1**.[2] We have



proposed the name "bond-stretch invertomers" for a pair of bond-stretch isomers, such as **1** and **2**, which are related by the inversion of two terminal groups.[1]

The finding that there is a local minimum for bond-stretched invertomer **2** on the PES for **1** is of purely theoretical interest, because **2** is calculated to be 2.4 kcal mol^{-1} higher in enthalpy than diradical **3**, which is also a local minimum. Therefore, the existence of the local energy minimum for bond-stretched invertomer **2** is unlikely to have any significance on the chemistry of **1**.

However, in the absence of the π bonding in **3**, a bond-stretched invertomer, analogous to **2**, might become the lowest energy intermediate on the PES for ring opening of a fluorinated cyclopropane. Herein we report the results of (6/6)CASPT2/6-311 + G(2d1f,2p)//(6/6)CASSCF/6-31G* calculations[3] which show that this is, indeed, the case for the ring opening of hexafluorocyclopropane (**4**). Moreover, the results of our calculations suggest that bond-stretched invertomer **5** may be the reactive intermediate in the previously reported halogenation of **4**.[4]

Our (6/6)CASSCF/6-31G* exploration of the PES for the ring opening of **4** found that **5** was by far the lowest energy intermediate. As shown in Figure 1, single-point

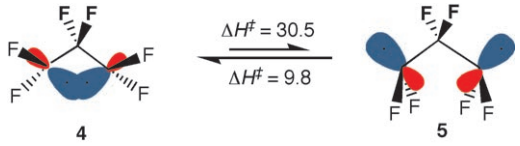


Figure 1. Hexafluorocyclopropane (**4**), its bond-stretched invertomer (**5**), and the activation enthalpies (kcal mol^{-1}) computed for their interconversion at 150 °C.

(6/6)CASPT2/6-311 + G(2d1f,2p) calculations give an enthalpy difference of 20.7 kcal mol^{-1} between hexafluorocyclopropane (**4**) and bond-stretched invertomer **5**. Single-point calculations in C_{2v} symmetry indicate that interactions between the atomic orbitals on the terminal carbon atoms stabilize the singlet state of **5** by 13.8 kcal mol^{-1} relative to the triplet state.[5]

Direct closure of **5** to form **4** is inhibited by the large barrier to inversion of the two CF_2 radical centers.[1,6] In addition, through-space and through-bond interactions[7a] both stabilize the in-phase combination of the two radical centers in **5**,[7b] thus creating a barrier to rotation about the bonds to the terminal CF_2 groups. The transition structure (TS) for closure of **5** to give **4** by rotation of the terminal CF_2 groups has a CASPT2 energy which is 2.3 kcal mol^{-1} higher than that of the C_{2v} TS for ring closure of **5** by simultaneous inversion of both CF_2 groups.

At the (6/6)CASSCF level the C_{2v} stationary point for ring closure of **5** by double inversion is actually an energy maximum on the global CASSCF PES. One of the two vibrations with imaginary frequencies breaks the C_{2v} symmetry and leads to a stationary point with only one imaginary frequency. This stationary point is the CASSCF transition structure for inversion of just one CF_2 group.

The inclusion of dynamic electron correlation at the CASPT2 level affects the PES for the ring closure of **5** to form **4** by significantly reducing the calculated barriers to inversion

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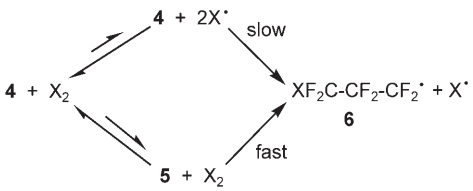
of only one or both CF_2 groups.[1,6f,8] On the CASPT2 PES, the energy maximum on the single inversion pathway for ring closure has almost the same energy as the diradical intermediate, with one terminal CF_2 group pyramidalized inward, as in **4**, and the other pyramidalized outward, as in **5**. On the CASPT2 PES this diradical is calculated to be 2.1 kcal mol^{-1} higher in energy than the C_{2v} transition structure for ring closure of **5** by simultaneous inversion of both CF_2 groups. Thus, our CASPT2 calculations predict that double inversion provides the lowest energy pathway for ring closure of **5** to **4**. The CASPT2 enthalpy barrier for this mode of ring closure at 150 °C is calculated to be 9.8 kcal mol^{-1}.[9]

With a calculated barrier to ring closure of about 10 kcal mol^{-1}, it seems that it might be possible to trap **5** chemically. The rate constant for ring closure at around 150 °C should be about 10^8 s^{-1}. If bimolecular trapping of **5** is barrierless, a 1 M concentration of the trapping agent should lead to the pseudo-first-order rate constant for trapping being on the order of 10^{10} s^{-1}, which is a factor of a hundred larger than the rate constant for ring closure.

If trapping really were two orders of magnitude faster than ring closure, the rate-determining step in the trapping of **5** would be the ring opening of **4**. Thus, at high concentrations of trapping agent, the rate of formation of the trapping product should become independent of the concentration of the trapping agent. Therefore, a kinetic study should provide a way of differentiating between the trapping of **5** and the reaction of the trapping agent with **4**, prior to ring opening of **4** to give **5**.

It is possible that bond-stretched invertomer **5** has already been trapped chemically. Yang et al. have reported that **4** reacts with halogen molecules at elevated temperatures to form 1,3-dihalo-1,1,2,2,3,3-hexafluoropropanes.[4] These reactions presumably involve the formation of radical **6** by one of the two pathways shown in Scheme 1, followed by the much faster reaction of **6** with X_2 to form the product.



Scheme 1.

Our CASPT2 calculations predict substantial barriers of 22.1 and 25.6 kcal mol^{-1} for the formation of **6** by the reaction of **4** with chlorine and bromine atoms, respectively. In addition, at least at the outset of the reaction of **4** with halogen molecules, the concentration of X• will be determined by the equilibrium constant for the dissociation of X_2 and, hence, will be very low.

In contrast, the formation of **6** by reaction of **5** with chlorine and bromine molecules is computed to be essentially barrierless, and the concentration of X_2 molecules will, at least initially, be many orders of magnitude larger than the concentration of X• atoms. Therefore, even though the barrier to the ring opening of **4** to give **5** is computed to be 30.5 kcal mol^{-1}, the preferred mechanism for the formation of **6** is predicted to consist of the ring opening of **4** to **5**, followed by the rapid reaction of **5** with halogen molecules.[10] At sufficiently high concentrations of halogen molecules, the barrierless reaction of **5** with X_2 should become so fast that the ring opening of **4** will be the rate-determining step. The rate of reaction will then become independent of both further increases in the X_2 concentration and of the identity of X_2.

Unfortunately, the dependence of the rates of the reactions of **4** on the concentrations of X_2 was not reported.[4] However, careful measurements of the initial rates of these reactions at sufficiently high halogen concentrations should reveal that the mechanism consists of a rate-determining ring opening of **4** to form the bond-stretched invertomer (**5**), which is then rapidly trapped by X_2.

The calculated barrier height of 30.5 kcal mol^{-1} for the ring opening of **4** to give **5** is considerably lower than that of 42.0 kcal mol^{-1} for the extrusion of difluorocarbene from **4**. The barrier height computed for the latter reaction is in reasonable agreement with the experimental value of $E_a =$ 38.6 kcal mol^{-1}, measured in the temperature range 253–276 °C.[11]

It has been previously suggested, based on the results of MP2/6-31G* calculations, that **5** actually lies on the reaction pathway for extrusion of difluorocarbene from **4**.[12] Our (6/6)CASSCF calculations also predict that the extrusion of CF_2 from **4** is a stepwise reaction, with the first step consisting of the stretching of just one C–C bond, which leads to the formation of **5** as an intermediate.[13] The changes in bond lengths that occur on passing from **5** to the transition structure for extrusion of CF_2 are depicted in Figure 2.

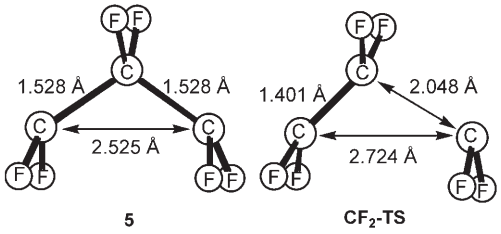


Figure 2. C–C bond lengths in the bond-stretched invertomer (**5**) and in the transition structure (**CF_2-TS**) for extrusion of difluorocarbene from **5** calculated with (6/6)CASSCF/6-31G* theory.

In summary, our calculations have identified bond-stretched invertomer **5** as a true intermediate on the potential-energy surface for the ring opening of hexafluorocyclopropane (**4**). The existence of **5** as an intermediate is due to a mixture of two factors: First, a substantial barrier, caused by the high energy required to simultaneously invert two CF_2 radical centers,[1,6] impedes direct closure of **5** to give **4**. Second, a combination of through-space and through-bond interactions between the inverted radical centers inhibits closure to give **4** through rotations about the C–C bonds in **5**.[7]

We propose that **5** is a plausible intermediate in bimolecular reactions of **4**, such as its halogenation.[4] It should be possible to test this hypothesis experimentally by investigating the dependence of the reaction rate on the concentration of the trapping agent. At sufficiently high concentrations, the ring opening of **4** to form bond-stretched invertomer **5** should become rate determining, and the rate of trapping should become independent of both the concentration and the identity of the trapping agent.

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