

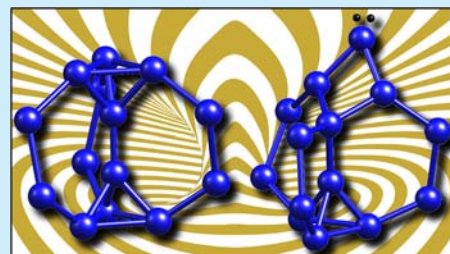
A Quantum Mechanical “Jack in the Box”: Rapid Rearrangement of a Tetrahedryl-Tetrahedrane via Heavy Atom Tunneling

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S Supporting Information

ABSTRACT: A bridged tetrahedryl-tetrahedrane (“TT”) was, theoretically, recognized as the holder of the chemical record for the shortest C–C single bond in a stable molecule. However, owing to its strained nature, this molecule is prone to rearrange to a carbene via ring contraction. Although TT was predicted to be stable to rearrangement at very low temperatures, our calculations find that, due to carbon quantum mechanical tunneling, even at 0 K it will immediately rearrange, with a half-life of only 4 ms. TT provides an excellent example of why tunneling effect should be considered in the stability analysis of a theoretically conceived molecule, even at cryogenic temperatures.



As in any other human enterprises, chemists are prone to look for chemical “world records”.¹ Among these, there is an academic interest in predicting and finding the shortest single C–C bond.^{2–11} The current (computationally predicted) record is held by a bridged tetrahedryl-tetrahedrane (“TT”), with a bond distance of only 1.31 Å¹² (calculated at the B3LYP/6-311G(d,p) level,¹² or 1.30 Å with the B1B95/6-31G(d) method used in this Letter; see Figure 1). This

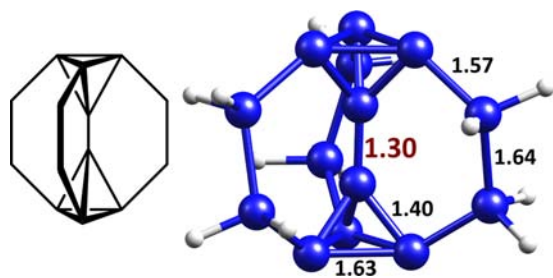


Figure 1. Line drawing and ball-and-stick depictions of “TT”, a bridged tetrahedryl-tetrahedrane (D_3 symmetry, with selected bond distances in Å). This putatively stable molecule holds the current theoretical record for the shortest predicted single C–C bond length.

molecule designed by Martínez-Guajardo et al. involves a synergism between the compression brought by three ethylene groups (the “iron maiden” effect⁶) and the enhanced s character of the carbons on the tetrahedranes.

In a recent study by Markopoulos and Grunenberg, a test of the stability of individual C–C bonds was conceived.¹³ In this method, any bond departing from an exponential trend in a graph of the relaxed force constant vs bond distance (similar to Badger’s rule)¹⁴ is expected to be unstable (or, more precisely, metastable). From all the molecules studied in this work, the one with the more evidently labile bond was seen to be none other than TT. The strain of the tetrahedrane moieties coupled

with the elongated ethylene bridges provides a strong driving force to open one of the tetrahedra—very much like a “Jack-in-the-box” toy—in a ring contraction reaction with an activation enthalpy (ΔH^\ddagger) of only 6.7 kcal/mol¹³ (calculated with B3LYP/6-31G(d),¹³ or $\Delta E^\ddagger = 5.9$ kcal/mol at the B1B95/6-31G(d) level as calculated in the present work). Despite the fact that this process generates a carbene, it is significantly exothermic ($\Delta E_{rx} = -105.4$ kcal/mol with B1B95/6-31G(d); see Figure 2).

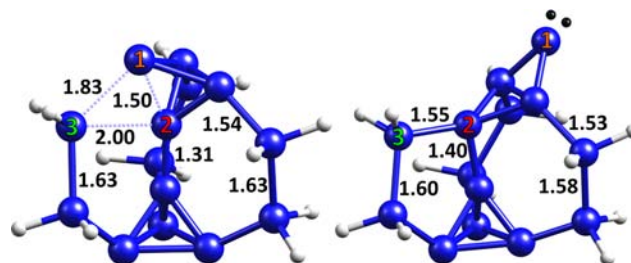


Figure 2. Transition state (TT^{TS1}) and product (TT²) of the ring contraction and carbene generation from TT, with selected C–C bond distances in Å.

Although the rearrangement barrier of TT is quite low, at cryogenic temperatures, where there is little thermal energy, TT should be stable to passage over the reaction barrier (where by “stable” we mean that it does not react at the specified conditions in a reasonable time). However, because of the high exothermicity of the rearrangement reaction, it has an early transition state with a narrow barrier.¹⁵ A tight barrier facilitates quantum-mechanical tunneling (QMT), even by “heavy” (i.e., non-hydrogen) atoms.^{16–18} The question that naturally arises is

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could the rearrangement of TT at cryogenic temperatures occur by carbon QMT?

In a provocative essay,¹⁹ Hoffmann, Schleyer, and Schaefer asked for “more realism” in the description of hypothetical molecules whose existence has been predicted by computational studies. They proposed two categories for those systems, “viable” and “fleeting”. The first considers the molecules that would withstand ambient conditions in a typical chemical laboratory environment; the second requires a molecule only to be a local minimum. Even though the barrier to rearrangement may be small, a molecule that is a local minimum should be stable at sufficiently low temperature.

We shall argue that possible rearrangement by QMT is an additional factor that must be taken into account in order to properly analyze the stability of a molecule. As we will see with TT, cryogenic temperatures are insufficient to protect a molecule from undergoing rapid rearrangement if it occurs by QMT *through* the reaction barrier, rather than by a thermally activated passage *over* it.

Many reactions involving tunneling by carbon have been observed experimentally and/or predicted theoretically.^{17,20–34} Among these are ring *expansions* of carbenes,^{17,29–32} or a recent case of carbene formation by a similar process.³³ However, to the best of our knowledge, the reverse reaction—a ring *contraction* producing a carbene,¹³ as in Figure 2—has never been suggested to occur through QMT. Therefore, in this work the calculation of the rate constant for carbene formation from TT by QMT was carried out.

The semiclassical rate constants for passage over the reaction barrier were computed with canonical variational transition state theory (CVT),³⁵ while the rate constants for multidimensional tunneling were computed using the small curvature tunneling (SCT) approximation.³⁶ Note that the SCT rate constants, as expressed here, include both semiclassical and QMT contributions.

The tunneling calculations were carried out with Polyrate.³⁷ All QM calculations were done with Gaussian09³⁸ (with Gaussrate³⁹ as the interface between Polyrate and Gaussian09), at the B1B95/6-31G(d) level of theory.⁴⁰ We are aware of the flaws of this basis set for the computation of barrier heights,⁴¹ but after careful comparisons with CCSD(T)-F12(b)/cc-pVTZ-F12//DSD-PBEh-P86/Def2-TZVP benchmark calculations,^{42–45} B1B95/6-31G(d) was found to be a fast and accurate method for this system (see Supporting Information (SI)).

Table 1 shows the rate constants (k) and half-life ($t_{1/2}$) for the ring contraction of TT at different temperatures. Evidently, at cryogenic conditions a classical “over the barrier” reaction would take eons. On the other hand, if QMT is included, even at absolute zero the reaction is predicted to occur in milliseconds ($t_{1/2}^{\text{SCT}} = 4$ ms)! Thus, TT, which might have been expected to be stable at low temperature,^{12,13,19} is actually predicted here to be unstable at any temperature, due to heavy atom tunneling.

The reason for such a swift QMT can be traced to the calculation of the tunneling limit (T_L) of the reaction:^{16–18}

$$T_L = w\sqrt{\Delta E^\ddagger m} \quad (1)$$

where m is the effective mass of the tunneling determining atom (“TDA”, in this case carbon 1 (see Figures 2 and 3) with $m = 12$ au), ΔE^\ddagger is the energy of activation (5.9 kcal/mol), and w is the half-height width of the barrier for the displacement of

Table 1. Rate Constants (in s^{-1}) and Half-Life (in s) for the Ring Contraction of TT, with and without Tunneling (SCT and CVT, respectively), at Selected Temperatures (in K)^a

T	k_{CVT}	k_{SCT}	$t_{1/2}^{\text{CVT}}$	$t_{1/2}^{\text{SCT}}$
10	6.2×10^{-104}	1.7×10^2	1.1×10^{103}	4.1×10^{-3}
20	5.6×10^{-46}	1.7×10^2	1.2×10^{45}	4.1×10^{-3}
50	5.5×10^{-11}	2.0×10^2	1.3×10^{10}	3.4×10^{-3}
75	4.0×10^{-3}	4.4×10^2	1.7×10^2	1.6×10^{-3}
100	3.7×10^1	3.1×10^3	1.9×10^{-2}	2.2×10^{-4}
150	3.9×10^5	1.4×10^6	1.8×10^{-6}	4.9×10^{-7}
200	4.2×10^7	8.7×10^7	1.7×10^{-8}	8.0×10^{-9}
250	7.0×10^8	1.2×10^9	9.9×10^{-10}	5.9×10^{-10}
300	4.7×10^9	7.0×10^9	1.5×10^{-10}	1.0×10^{-10}

^aSince by symmetry there are six equivalent ring contractions (carbene generation from three possible vertices of each of the two tetrahedranes), the rate constants that appear in the table are the polyrate outputs multiplied by a factor of 6.

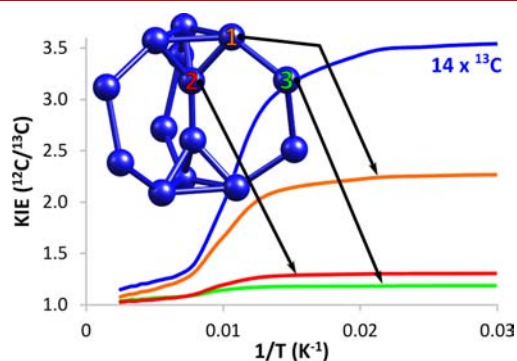


Figure 3. $^{12}\text{C}/^{13}\text{C}$ kinetic isotope effect for the ring contraction of TT for three isotopomers containing one ^{13}C at the depicted positions, and for the total substitution of the 14 carbon atoms.

the TDA (0.27 Å; see Table S1 and Figure S3 of the SI). As a rule of thumb, a tunneling limit below 3 indicates a molecule with chances to react by QMT from its lowest vibrational level.¹⁷

The resulting T_L for TT is 2.2, which is clearly below the threshold for tunneling. As explained before, the key factor for tunneling is the barrier width, the only term in eq 1 outside the square root. As the probability of tunneling is inversely proportional to the exponential of T_L ,¹⁷ the narrow barrier on the ring contraction of TT enables the reaction even at 0 K. Other similar systems but with wider barriers (hence with bigger T_L) have been computed to be stable at low temperatures, and unreactive by a QMT mechanism (see SI).

Given that a strong tunneling effect is usually associated with a large kinetic isotope effect (KIE), calculations of the KIEs for ^{13}C isotopic substitution at different carbons of TT were undertaken. As expected, the “future carbene” atom (carbon 1 in Figures 2 and 3) is the tunneling determining atom, with a KIE reaching a stunning value of 2.26 at low temperature. This value can be compared to the conventional ^{13}C KIE at C1 of 1.08 for passage over the reaction barrier at room temperature. Atom 1 has the largest motion in the rearrangement, explaining its extremely high KIE.

Carbons 2 and 3 (i.e., the vertex of the tetrahedron inside the cage and the bridging atom; see Figures 2 and 3) also have high KIEs of 1.30 and 1.18, respectively, at low T . However, these KIEs are much lower than the KIE of C1. All of the other carbons do not have significant KIEs, indicating that their

masses do not affect the tunneling probability, as their displacements in the rearrangement reaction are negligible. Replacing all 14 carbons with ^{13}C gives an SCT KIE of 3.56. This value is close to 3.50, the product of the KIE for the substitution of the individual C1, C2, and C3 (see Figure 3).

Interestingly, the reaction does not end at the TT^2 stage. This carbene is still highly strained at the remaining tetrahedrane and can proceed to a second ring contraction forming a bis-carbene (TT^3 ; see Figure 4), with $\Delta E^\ddagger = 5.8$ kcal/mol and $\Delta E_{\text{rx}} = -76.9$ kcal/mol.

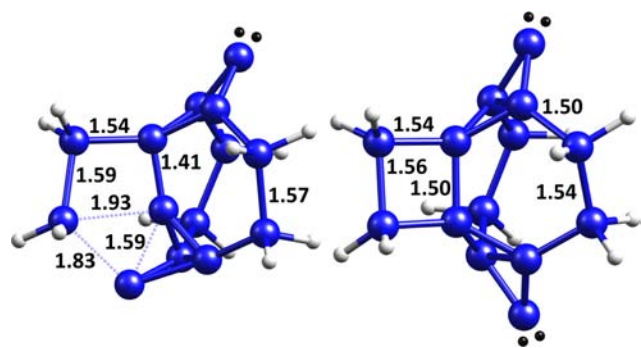


Figure 4. Transition state ($\text{TT}^{\text{TS}2}$) and product (TT^3 , of C_2 symmetry) for the second ring contraction and carbene generation from TT^2 , with selected bond distances in Å.

This second reaction is calculated to be almost as fast as the first ring contraction, with $t_{1/2}^{\text{SCT}} = 6$ ms. The T_L is virtually the same, 2.2, with a slightly lower barrier for the second rearrangement (5.8 vs 5.9 kcal/mol), but a slightly wider barrier ($w = 0.26$ Å vs 0.27 Å; see eq 1 and Table S1 of the SI). From Table 2 it is possible to see that, again, the over the

Table 2. Rate Constants (in s^{-1}) and Half-Life (in s) for the Ring Contraction of TT^2 , with and without Tunneling (SCT and CVT, respectively), at Selected Temperatures (in K)^a

T	k_{CVT}	k_{SCT}	$t_{1/2}^{\text{CVT}}$	$t_{1/2}^{\text{SCT}}$
10	2.6×10^{-96}	1.1×10^2	2.7×10^{95}	6.4×10^{-3}
20	1.5×10^{-42}	1.1×10^2	4.7×10^{41}	6.4×10^{-3}
50	4.5×10^{-10}	1.4×10^2	1.5×10^9	4.9×10^{-3}
75	9.5×10^{-3}	3.4×10^2	73	2.1×10^{-3}
100	48	2.5×10^3	1.4×10^{-2}	2.7×10^{-4}
150	2.8×10^5	8.4×10^5	2.5×10^{-6}	8.3×10^{-7}
200	2.3×10^7	3.9×10^7	3.1×10^{-8}	1.8×10^{-8}
250	3.3×10^8	4.6×10^8	2.1×10^{-9}	1.5×10^{-9}
300	2.0×10^9	2.5×10^9	3.4×10^{-10}	2.8×10^{-10}

^aUnlike the six possible ring contractions on $\text{TT} \rightarrow \text{TT}^2$ (see footnote in Table 1), in this case there is only one possible reaction at the position shown in Figure 4 ($\text{TT}^2 \rightarrow \text{TT}^3$), and therefore the rate constants of the table are the outputs of Polyrate, without any multiplicative factor. The other two vertices of the tetrahedrane will not react, as they have a much higher ΔE^\ddagger for the alternative ring contractions (13.8 kcal/mol). No other alternative rearrangements were found to be viable at low temperatures.

barrier reaction is impossible at cryogenic conditions, but the heavy atom tunneling mechanism permits an almost instantaneous second carbene generation. No further intramolecular rearrangements were found after TT^3 formation at low temperature.

Therefore, we predict that successful generation of TT would swiftly lead to the formation of TT^3 (at least in gas phase at 0 K, where no other plausible reaction was theoretically detected). Consequently, due to its short lifetime, it cannot be claimed that TT holds the record for the shortest C–C single bond in a *stable* molecule.¹²

In summary, our calculations predict that rearrangement of a bridged tetrahedryl-tetrahedrane (TT) to bis-carbene (TT^3) will occur rapidly, with a half-life on the order of milliseconds even at 0 K by carbon tunneling. Consequently, we predict that QMT will make it impossible to isolate TT under any conditions, despite the fact that calculations which do not include tunneling indicate that this molecule would be stable at low temperatures. Thus, the possibility of QMT by “heavy atoms” opens a new and potentially important dimension in the assessment of the stability¹⁹ of highly strained molecules.

■ ASSOCIATED CONTENT

§ Supporting Information

Discussion on the tunneling probability of other bridged tetrahedryl-tetrahedranes, Polyrate outputs and example of input, benchmark, and XYZ geometries. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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