Supporting Information

How Small Can a Catenane Be, if We Consider Quantum Tunnelling?

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All the geometries and Gaussian output files are available on the ioChem-BD platform for computational chemistry and materials science teams, at the following link: https://iochem-bd.bsc.es/browse/review-collection/100/446103/f7f3084765a90cd35352cc49

Electronic structure method

The selection of the electronic structure method required careful consideration of the state of the system when breaking the C-C bond. At large C-C distances, when the molecule is fragmented, the system necessarily is a diradical, with one unpaired electron on each terminal methylene. However, at the transition state the bond length is at an intermediate distance, near the crossing between the close-shell singlet (CSS) and the open-shell singlet (OSS) surfaces.

When testing several functionals for the ring opening on strained catenanes, we observed that some of them provided an OSS state at the transition state (such as M06-2X), while most others indicated that CSS was the lowest energy state (such as PBE, the selected functional). The correct selection of the functional is therefore crucial in this situation to obtain a qualitatively correct potential energy surface. In previous studies[1] we concluded that, despite the possible spin contamination, unrestricted CCSD(T) can provide accurate energies for reactions in the OSS surface, thus offering a good benchmark for the functional selection in terms of threshold energies and electronic state.

On the other hand, the size of the studied molecules makes it impossible to compute canonical CCSD(T) with a relevant basis set. For the $\mathbf{R_{10}R_{10}}$ system, we could compute CCSD(T)/cc-pVDZ, which is not enough for accurate energies, but it is useful to establish the ground state structure at the transition state. Using the geometry at the TPSSh/6-31g(d) level, coupled cluster clearly indicates that CSS is the correct energy surface in this section of the reaction, with a threshold energy of 14 kJ.mol^{-1}, against 28 kJ.mol^{-1} for the OSS. This was obtained with uCCSD(T) using uHF as reference, which provides a notoriously wrong OSS state 48 kJ.mol^{-1} lower than the CSS (a reason why functionals with high exact exchange are problematic for this particular reaction). The T1 diagnostics were below 0.01, further justifying the use of CSS CCSD(T) as a benchmark. We decided to use DLPNO-CCSD(T1)/cc-pVQZ with tightPNO for the single point reference energies, as it provides the best balance between accuracy and tractable computational time.

In the same sense, due to the large computational cost of SCT, rates with a heavy functional/basis set combination were intractable for systems of this size. Therefore, upon comparison with the DLPNO-CCSD(T1) benchmark, we tested several functionals with the small 6-31G(d) basis set (see Table **S1**). Clearly DFT tends to overbind, with worse results usually obtained with hybrid functionals (except for B3LYP and M06). For the sake of computational cost, we decanted for the best GGA functional of the set, i.e. PBE. In any case, to enhance the accuracy, the PES was corrected with the ISPE method using DLPNO-CCSD(T1), as already explained in the main text.

Table S1. Threshold energies and errors in kJ.mol^{-1} for several functionals with 6-31G(d) basis set, and the benchmark reference with DLPNO-CCSD(T1)/cc-pVQZ/tightPNO//TPSSh/6-31g(d) for $\mathbf{R_{10}R_{10}}$.

	$\Delta E^{\ddagger}$	Err
B3LYP	9	2
PBE	12	6
M06	13	6
BB95	13	7
TPSS	15	9
B98	16	9
TPSSh	21	14
M06-2X	23	17
wB97XD	26	19
PBE0	27	21
B1B95	32	25
MN15	37	31
DLPNO-CCSD(T1)	6.4	

1 Y. Avivi, J. J. Santoyo-Flores, T. Schleif and S. Kozuch, Cryogenic Rearrangements of Spiroheptadiyl: Light- or Heavy-Atom Quantum Tunneling?, *J. Phys. Chem. Lett.*, 2024, 163–167.

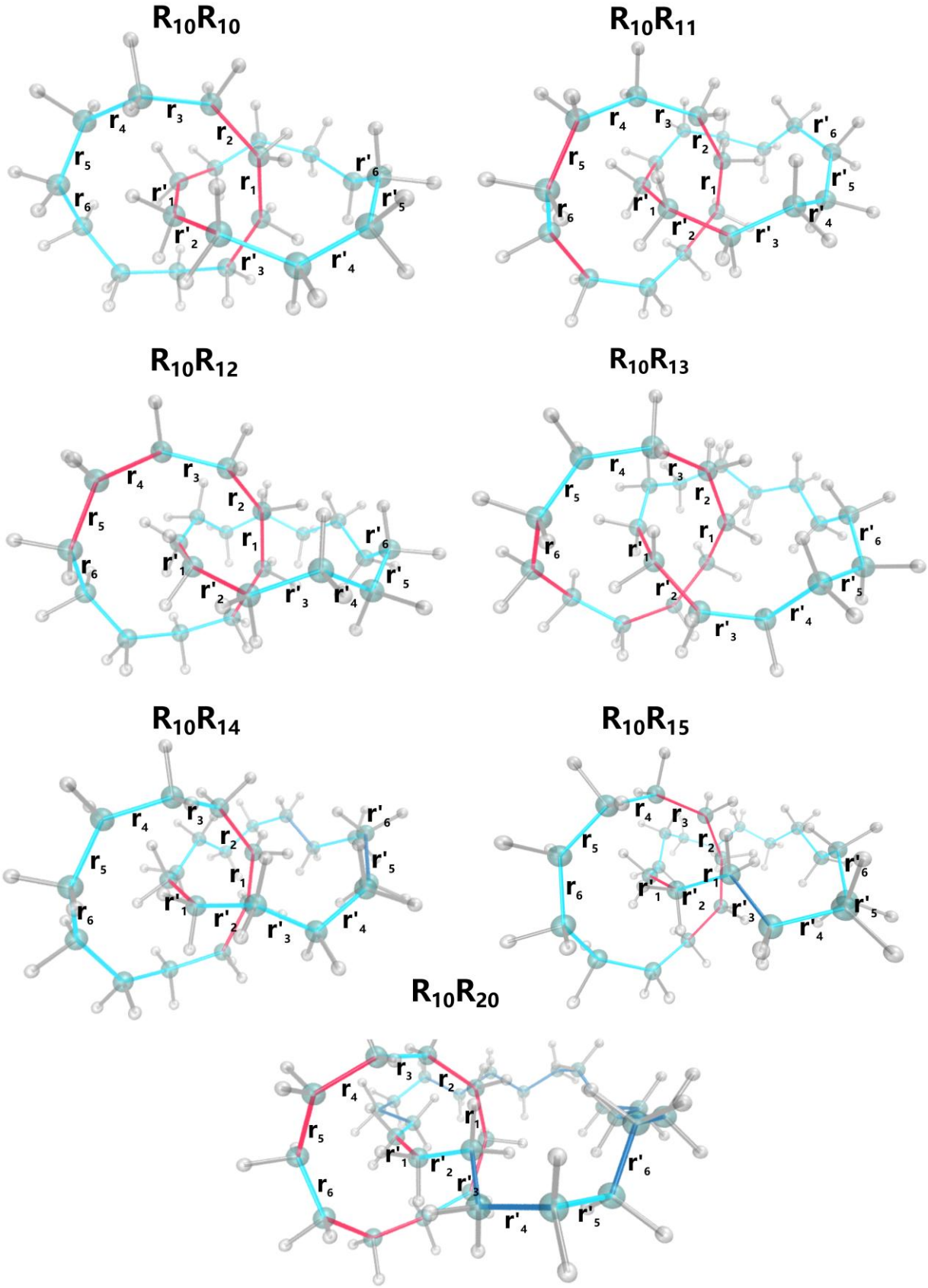

Figure S1. Color scale for the C–C bond lengths of $\mathbf{R_{10}R_m}$ structures within the following intervals: dark blue between 1.30 and 1.55 Å, cyan between 1.55 Å and 1.63 Å, and red for bond lengths exceeding 1.63 Å.

Table S2. C-C bond lengths (Å) for the optimized structures of $R_{10}R_m$.

System	R_{10}						R_m					
	r_1	r_2	r_3	r_4	r_5	r_6	r'_1	r'_2	r'_3	r'_4	r'_5	r'_6
$R_{10}R_{10}$	1.75	1.66	1.60	1.61	1.61	1.61	1.76	1.64	1.60	1.63	1.63	1.59
$R_{10}R_{11}$	1.70	1.65	1.60	1.63	1.63	1.60	1.76	1.66	1.59	1.61	1.60	1.58
$R_{10}R_{12}$	1.68	1.64	1.61	1.64	1.64	1.61	1.73	1.64	1.58	1.58	1.58	1.57
$R_{10}R_{13}$	1.65	1.66	1.64	1.61	1.60	1.64	1.76	1.64	1.57	1.56	1.57	1.56
$R_{10}R_{14}$	1.67	1.65	1.62	1.62	1.62	1.62	1.75	1.62	1.58	1.56	1.55	1.55
$R_{10}R_{15}$	1.64	1.65	1.64	1.61	1.64	1.65	1.79	1.61	1.57	1.55	1.56	1.56
$R_{10}R_{20}$	1.67	1.66	1.63	1.66	1.66	1.62	1.71	1.56	1.54	1.55	1.55	1.55

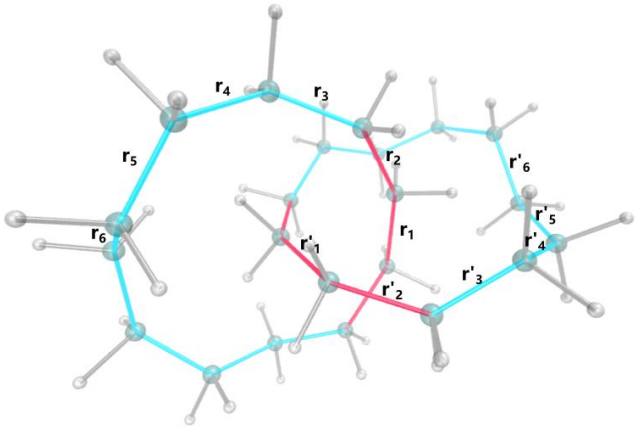

Figure S2. Color scale for the C–C bond lengths of $R_{11}R_{11}$ within the following intervals: dark blue between 1.30 and 1.55 Å, cyan between 1.55 Å and 1.63 Å, and red for bond lengths exceeding 1.63 Å.

Table S3. C-C bond lengths (Å) for $R_{11}R_{11}$.

	$R_{11}R_{11}$		$R_{11}R_{11}$
r_1	1.70	r'_1	1.71
r_2	1.65	r'_2	1.64
r_3	1.60	r'_3	1.60
r_4	1.60	r'_4	1.60
r_5	1.60	r'_5	1.60
r_6	1.59	r'_6	1.59

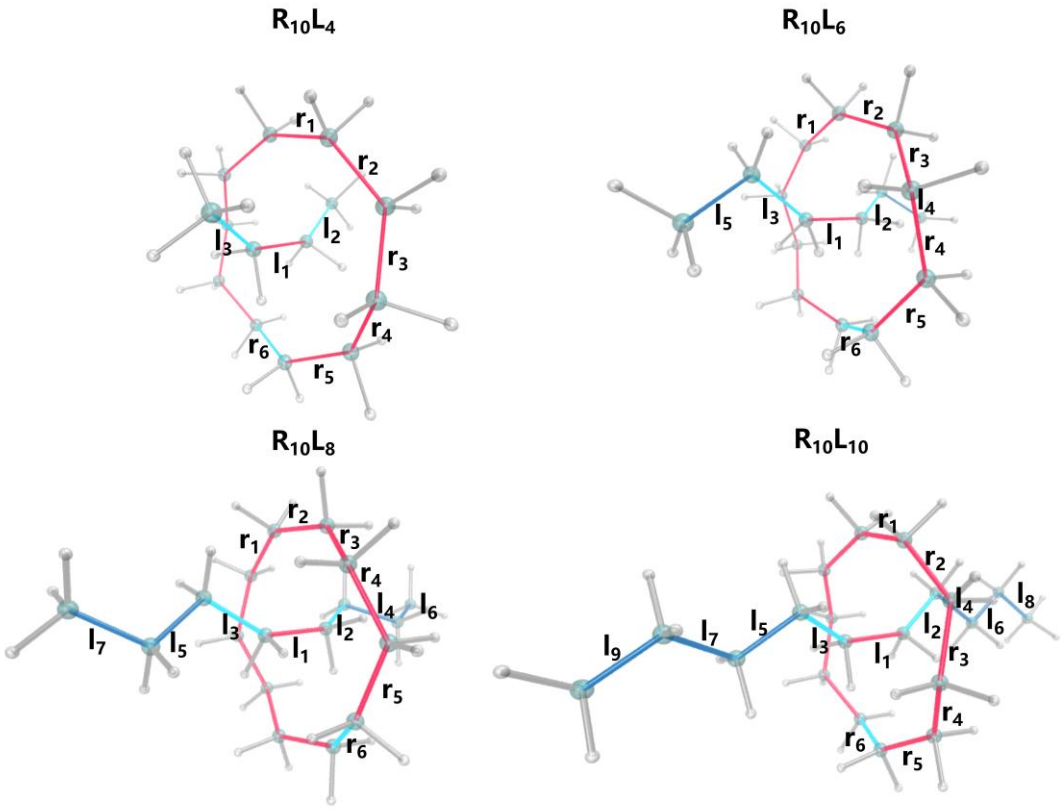

Figure S3. Color scale for the C–C bond lengths of $\mathbf{R_{10}L_m}$ within the following intervals: dark blue between 1.30 and 1.55 Å, cyan between 1.55 Å and 1.63 Å, and red for bond lengths exceeding 1.63 Å.

Table S4. C-C bond lengths (Å) for $\mathbf{R_{10}L_m}$.

	$\mathbf{R_{10}}$						$\mathbf{L_m}$								
$\mathbf{R_{10}L_4}$	1.67	1.66	1.64	1.63	1.63	1.63	1.67	1.56	1.56						
$\mathbf{R_{10}L_6}$	1.67	1.66	1.64	1.63	1.63	1.63	1.68	1.57	1.57	1.54	1.54				
$\mathbf{R_{10}L_8}$	1.67	1.66	1.64	1.63	1.63	1.63	1.68	1.57	1.57	1.54	1.54	1.53	1.53		
$\mathbf{R_{10}L_{10}}$	1.67	1.66	1.64	1.63	1.63	1.63	1.68	1.57	1.57	1.54	1.54	1.54	1.54	1.53	1.53

Table S5. ZPE included threshold energies in kJ.mol^{-1}, imaginary frequencies at the transition state for C-C bond breaking in $\mathbf{R_{10}}$, and tunnelling and semi-classical rate constants in s^{-1} from ground state QT (10 K) and at liquid N_2 conditions (77 K) for catenanes' decomposition of the small ring.

	$\Delta E^{\ddagger}$	$\nu^{\ddagger}$	10 K		77 K	
			k_{QT}	k_{SC}	k_{QT}	k_{SC}
$\mathbf{R_{10}R_{11}}$	29.9	264	10^{-11}	10^{-147}	1×10^{-7}	7×10^{-7}
$\mathbf{R_{10}R_{12}}$	41.9	247	10^{-38}	10^{-212}	10^{-16}	10^{-17}
$\mathbf{R_{10}R_{13}}$	55.0	243	10^{-59}	10^{-281}	10^{-25}	10^{-26}
$\mathbf{R_{10}R_{14}}$	48.8	240	10^{-43}	10^{-246}	10^{-21}	10^{-21}
$\mathbf{R_{10}R_{15}}$	98.3	386	10^{-42}	10^{-289}	10^{-26}	10^{-27}
$\mathbf{R_{10}R_{20}}$	71.2	214	-	-	10^{-37}	10^{-36}
$\mathbf{R_{10}L_4}$	65.5	220	-	-	10^{-32}	10^{-32}
$\mathbf{R_{10}L_6}$	65.2	216	-	-	10^{-33}	10^{-33}
$\mathbf{R_{10}L_8}$	65.8	215	-	-	10^{-33}	10^{-33}
$\mathbf{R_{10}L_{10}}$	65.7	217	-	-	10^{-33}	10^{-33}

Table S6. Temperature (k), tunnelling and semi-classical rate constants in s^{-1} for $\mathbf{R_{11}R_{11}}$

T (K)	$\boldsymbol{k_{QT}}$	$\boldsymbol{k_{SC}}$
5	7×10^{-12}	10^{-242}
10	7×10^{-12}	10^{-115}
20	7×10^{-12}	10^{-52}
30	1×10^{-11}	10^{-31}
40	3×10^{-11}	10^{-20}
50	2×10^{-10}	6×10^{-14}
60	2×10^{-8}	1×10^{-9}
70	8×10^{-6}	1×10^{-6}
77	3×10^{-4}	8×10^{-5}

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C    -3.928249   -0.704565   -0.062713
C    -1.884851    1.327244    2.350468
H    -2.069000    2.057591    3.165951
H    -1.906147    0.350693    2.872151
C    -0.748019   -1.674747   -1.966203
H    -0.377358   -2.098867   -2.921449
H    -0.827008   -2.547660   -1.292288
C     0.454369   -0.712909   -1.553920
H     0.396177    0.106517   -2.285339
C    -3.726573    0.837258    0.135994
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H    -3.465789   -1.277058    0.757013
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H    -4.323189   -1.053198   -2.163750
H    -4.017454    1.338725    2.235364
H     1.571613   -0.944038    0.238832
H    -2.146632   -0.092584   -2.642976
H    -2.476755   -1.690301   -3.249347
H     1.345686   -1.292181   -1.883779
H    -1.281859    1.139432   -1.717816
C     4.096301    0.633668   -0.738659
H     4.468013    0.513441   -1.775639
H     4.978817    0.975440   -0.161964
C     3.338903   -1.094401    1.238151
H     4.239032   -1.363902    1.825853
C     3.798877   -0.841225   -0.244613
H     3.116702   -1.335483   -0.955083
H     4.766600   -1.360829   -0.391224
C     1.878744    2.113034   -1.681638
H     1.842487    1.321108   -2.449688
C    -1.175769   -0.528836    0.414809
C     0.439201    2.386987   -1.047808
H     0.633974    2.975540   -0.134183
H    -0.020608    3.120407   -1.746615
C     3.150714    1.911851   -0.739977
H     3.856203    2.718527   -1.019805
H     2.870107    2.154947    0.300011
C     2.297740   -2.239311    1.621955
H     2.823922   -3.200037    1.459159
C    -0.823549    1.457864   -0.777595
H    -1.529383    2.095879   -0.236375
C    -0.481544   -1.687429    1.265176
C     0.838783   -2.544552    1.035780
H    -1.702493   -0.947056   -0.411557
H    -1.885795   -0.084274    1.079746
H    -0.484227   -1.379813    2.327007
H    -1.286997   -2.454063    1.202622
H     2.086649    3.037317   -2.254336
H     2.998105   -0.145228    1.676131
H     0.928559   -2.807966   -0.032673
H     0.603459   -3.506919    1.537011
H     2.188865   -2.156951    2.721410
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