Supplementary Information Electronic structure of norbornadiene and quadricyclane

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1 Orbitals



Figure S1: Orbitals (isosurface value of 0.05) for CASSCF(4,4)/p-cc-(p)VDZ at the NBD geometry. We use the same labelling as Fig. 2 in the main text

In Figure S1, we show the orbitals in NBD for CASSCF(4,4), which match Fig. 2 in the main text. For the CASSCF(2,2)/p-cc-(p)VDZ calculations, as shown in Figu. S2, the state-averaged (SA) natural orbitals do not resemble the orbitals of the (4,4) active space. This is due to the effect of the S₂ state, which is not well described, adding asymmetry. If we look at the natural orbitals for the S₀ state (or the S₁ state), then we can see the more familiar shapes, akin to the B_1 and B_2 orbitals in the (4,4) active space. The asymmetry in the orbitals does not affect the calculations — the two sets of orbitals are simply a rotation of each other.



Figure S2: Orbital (iso-surface value of 0.05) for CASSCF(2,2)/p-cc-(p)VDZ at the NBD geometry. On the right, we show the state-averaged (SA) natural orbitals, which exhibit pronounced asymmetry. The state-specific orbitals for the S_0 state (left, S_1 state gives similar results), do not show this asymmetry, and look much closer to Fig. S1.

2 Geometry parameters

Table S1: Geometry parameters for ground state optimised geometries, calculated using CASSCF and XMS-CASPT2 for various basis sets and active spaces. All geometries are C_{2v} , making $r_{rh} = 0$. The reference calculations (MP2/aug-cc-pVQZ) are taken from our previous work.¹ All distances in Ångström. The (4,3) and (4,4) active spaces are unstable around the QC ground state minimum, so those results are not included.

			QC		NBD	
Basis	Active space	Method	r _{cc}	r _{db}	<i>r</i> ₁₂	<i>r</i> ₁₄
p-cc-(p)VDZ	(2,2)	CASSCF	1.549	1.530	2.476	1.330
		XMS-CASPT2	1.518	1.555	2.473	1.365
		MRCI	1.535	1.538	2.474	1.339
	(4,3)	CASSCF			2.472	1.332
		XMS-CASPT2			2.474	1.365
	(4,4)	CASSCF			2.474	1.352
		XMS-CASPT2			2.483	1.356
ANO-L-VTZ(p)	(2,2)	CASSCF	1.552	1.525	2.470	1.322
_		XMS-CASPT2	1.503	1.544	2.455	1.351
aug-cc-pVQZ	HF	MP2	1.515	1.538	2.462	1.339

3 Excitation energies

Table S2 shows the vertical excitation energies for S_1 and S_2 , calculated from the NBD ground state. We also show the experimental value (5.25 eV). Most correlated methods predict the excitation energy in the right ballpark, with energies in the 5.25 ± 0.4 eV range. We note that the steeply sloped nature of this state could significantly affect the excitation energies, as a small displacement of the nuclear geometry leads to a relatively large change in excitation energy. As we use the same geometries (MRCI(2,2) for correlated methods, CASSCF(2,2) for non-correlated) across all comparisons, the calculations are not at the exact minimum for each of the methods, which could affect the excitation energy. Of particular note are the values for CASSCF(4,4), which is over 2 eV higher than the predictions of the other methods, and MRCI(4,4), which fails to significantly correct for the errors in CASSCF(4,4). SAC-CI calculations were performed using the Gaussian 16 package.²

Table S2: Calculated vertical excitation energies in NBD in eV. Experimentally, the state is posited to have a vertical excitation of \approx 5.25 eV, but the dissociative nature and lack of oscillator strength make this assignment difficult. All calculations are performed on MRCI(2,2)/p-cc-(p)VDZ ground state minimum geometry, except CASSCF calculations, which are performed on CASSCF(2,2)/p-cc-(p)VDZ geometry. The MP2/aug-cc-pV6Z value is taken from Cooper *et al.*.¹ Values next to CASPT2 in brackets indicate shift values, with IPEA indicating that the IPEA shift was used with the recommended value of 0.25 E_h. (2,2) and (4,4) active space calculations are state-averaged over three states, and (4,3) over four. ANO-L-VTZ(p) indicates an ANO-L-VTZP basis on the carbon atoms and an ANO-L-VTZ basis on the hydrogens. For the (4,3) active space, the two energies are from the 1¹A₂ and 2¹A₁ states, ignoring the 1¹B₂ state.

Basis (n,m) Meth		Method	$S_1 2ud0\rangle$	$S_2 2020\rangle$
Exp.			5.25	
p-cc-(p)VDZ	(2,2)	CASSCF	5.96	11.24
1 1/		MS-CASPT2 (0.2i)	4.85	8.55
		MS-CASPT2 (IPEA, 0.2i)	5.21	8.84
		XMS-CASPT2 (0.1i)	5.40	7.71
		XMS-CASPT2 (0.2i)	5.41	7.85
		XMS-CASPT2 (0.4i)	5.43	8.44
		MRCI	5.74	10.34
		MRCI+Q (DV1)	5.68	9.89
		MRCI+Q (DV2)	5.66	9.69
		MRCI+Q (DV3)	5.62	9.26
		MRCI+Q (Pople)	5.63	9.40
		QD-NEVPT2	5.36	8.14
		XMC-QDPT2	5.44	8.09
		HCI(20, 80, $\epsilon_1 = 10^{-4}$)	5.83	
		SHCI(20, 80, $\epsilon_1 = 10^{-4}$, $\epsilon_2 = 10^{-7}$)	5.72	
(4,3)		CASSCF	6.09	8.18
		XMS-CASPT2 (0.2i)	5.30	7.85
(4,4)		CASSCF	7.55	8.00
		XMS-CASPT2 (0.2i)	5.01	8.01
		MRCI	6.47	8.13
		MRCI+Q (DV1)	6.01	8.20
		MRCI+Q (DV2)	5.83	8.22
		MRCI+Q (DV3)	5.47	8.25
		MRCI+Q (Pople)	5.59	8.24
	HF	LR-CC3	5.56	
		LR-CCSD	5.70	
		LR-CC2	5.46	
		SAC-CI	5.64	
aug-cc-pVTZ	HF	LR-CCSD	5.57	
		LR-CC2	5.34	
ANO-L-VTZ(p)	(2,2)	CASSCF	5.93	11.19
· T /		XMS-CASPT2 (0.2i)	5.28	7.66
ANO-L-VQZP	(2,2)	CASSCF	5.89	11.15
-		XMS-CASPT2 (0.2i)	5.26	7.66
aug-cc-pV6Z	HF	ADC(2)	5.34	

4 LIIC geometries



Figure S3: Carbon-carbon distance coordinates for the two LIICs used in the (r_{cc} , r_{rh})-plane, with key geometries labelled. All geometries are calculated at CASSCF(2,2)/p-cc-(p)VDZ level. The projection of the two branching plane coordinates *X* and *Y* into the plane are also shown (cf Fig. 12, main text).

In Fig. S3, we show the two different LIICs. The $QC\leftrightarrow S_1/S_0$ MECI \leftrightarrow NBD LIIC (solid purple line) travels straight between the minima and the conical intersection, conserving C_2 symmetry (approximately, as calculations are run without symmetry turned on). For the S_1/S_0 MECI \leftrightarrow S₁ minimum \leftrightarrow NBD LIIC, the first part of the pathway traverses from the conical intersection to the S₁ minimum, maintaining (approximate) C_2 symmetry. The second part of the pathway holds $r_{rh} = 0$, maintaining C_{2v} symmetry. From here, it is clear that we do not need to plot the QC \leftrightarrow S₁/S₀ MECI on both pathways.

5 Conical intersections



Figure S4: Branching plane X and Y vectors from S_1/S_0 MECI, optimised at XMS-CASPT2(2,2)/p-cc-(p)VDZ level. These vectors are very similar to the CASSCF(2,2) vectors shown in the main text, and all other methods tested here.



Figure S5: S_1/S_0 MECI geometries for all combinations of CASSCF, MRCI, and XMS-CASPT2, and the (2,2) and (4,4) active spaces overlaid. All geometries show approximately the same distortions from the ground state minima.

Firstly, we show the branching plane vectors from XMS-CASPT2(2,2)/p-cc-(p)VDZ in Fig. S4. These compare well with the CASSCF(2,2) vectors shown in the main text, with only very minor changes in the direction of the vectors. All methods also give very similar optimised geometries, as discussed in Table 2 in the main text. The geometries are shown superimposed in Fig. S5. There are minor differences (especially in the hydrogens attached to the four-carbon ring), but the overall features of the geometry are replicated in all methods.



Figure S6: Appropriateness of local linear approximation in the S_1/S_0 conical intersection: Analytical local linear representation (purple and light blue surfaces) against CASSCF(2,2) (rose and green surface) calculations inside the branching plane. The agreement is excellent, demonstrating that the local linear approximation is reasonable in the plotted region. Parameters taken from SA(3)-CASSCF/p-cc-(p)VDZ optimised geometry. Square surfaces are the *ab initio* results, the round surfaces the local linear representation.



Figure S7: Appropriateness of local linear approximation in the S_1/S_0 conical intersection: Calculated *ab initio* (solid purple) energies vs analytical local linear representation (dashed rose) as a function of polar angle θ at a distance of 0.02 Å around the S_1/S_0 MECI. Left: Energies and MECI calculated at SA(3)-CASSCF/p-cc-(p)VDZ level. Right: Energies and MECI calculated at XMS-CASPT2(2,2)/p-cc-(p)VDZ level. For both calculations, the analytical representation matches the calculated energies well, with only a slight underestimation. One can see the difference in 'single-path' vs 'bifurcating' intersections by the small minimum on the lower surface at $\theta \approx \frac{7\pi}{4}$. The θ is defined to be 0 along the positive X direction, and $\frac{\pi}{2}$ along the positive Y direction.

The energies in the branching plane are approximated according to the formula taken from the original work of Fdez.-Galván et al.,³

$$E^{\pm}(r,\theta) = \delta_{gh} r \left(\sigma \cos(\theta - \theta_s) \pm \sqrt{1 + \Delta_{gh} \cos(2\theta)} \right)$$

where E^{\pm} are the energies of the two states relative to the minimum energy crossing point, r and θ are the polar distance and angle, and δ_{gh} , Δ_{gh} , σ and θ_s are various parameters taken from the *ab initio* calculation at the optimised geometry (more details in Fdez.-Galvan et al.³).

For small r, these provide an excellent approximation of the local potential energy surfaces around the conical intersection. This can be seen clearly in Figs. S6 and S7, which compare the energies of *ab initio* calculations to the local linear representations. Figure S6 shows the linear representation (the two circular surfaces) and the energies of *ab* initio calculations (the square surfaces). Clearly, the two surfaces are almost on top of one another. This might be easier to see in Fig. S7, which show the potential energies on a circular trip around the minimum energy conical intersection (at r = 0.02 Å). Here, the agreement between the analytical representation and the energies calculated using *ab initio* methods is clearly very good.



Figure S8: Local linear approximations to the energy in the branching plane around the S_1/S_0 MECI geometries, optimised for CASSCF, XMS-CASPT2, and MRCI with both the (2,2) and (4,4) active spaces (columns represent methods, rows active spaces). S_1 is shown in light blue, S_0 in purple. The values *P* and *B* are discussed in the main text and are found using the methods of Fdez.-Galvan *et al.*. The NBD ground state minimum is roughly towards positive *X* and negative *Y*, whereas the QC ground state minimum is towards negative *X* and negative *Y*. To the naked eye, all methods show a similar energy landscape in the branching plane except CASSCF(4,4) (bottom left), which shows a slightly more tilted geometry with a less obvious second minimum. These plots are shown with energy in eV and distance in Ångström.

In Fig. S8, we show the local linear representation of the energies in the branching plane of the S_1/S_0 MECIs for all combinations of the (2,2) and (4,4) active space and SA(3)-CASSCF, XMS-CASPT2, and MRCI. Almost all methods agree about the rough shape of the intersection, with a notable ridge approximately along the X = 0 line. The notable exception is CASSCF(4,4), which gives a more slanted overall intersection, with a shallower minimum towards the negative X direction (towards QC).

5.1 The S_2/S_1 conical intersection



Figure S9: Energies in the branching plane of S_2/S_1 conical intersection, using the local linear representation³. This is a peaked, bifurcating intersection. The branching plane vectors are shown in Figure S10, with *X* breaking the symmetry and *Y* preserving it. The conical intersection was optimised using XMS-CASPT2(4,4)/p-cc-(p)VDZ. An illustrative trajectory is shown, which would travel from NBD to the S_1/S_0 conical intersection, missing the S_2/S_1 conical intersection



Figure S10: Branching plane vectors for the S_2/S_1 conical intersection, optimised using XMS-CASPT2(4,4)/p-cc-(p)VDZ. The X vector is a rhombic displacement, which takes the molecule almost directly to the S_1/S_0 conical intersection, while the Y vector is very similar to the displacement vector from NBD to QC. All vectors are almost entirely within the plane of the figure.

Finally, we mentioned the presence of a S_2/S_1 conical intersection. When using XMS-CASPT2(4,4)/p-cc-(p)VDZ (it does not exist in CASSCF(2,2)), the intersection can be found at (r_{cc} , r_{rh} , r_{db}) \approx (2.01, 0, 1.48) Å, close to the S_1 minimum. Figure S9 shows the branching plane energies for this intersection, calculated using the same method as in the main text³. It is clear that this is a peaked intersection with clear bifurcating character. By looking at the vectors in the branching plane (shown in Fig. S10), we can identify the X direction as breaking the symmetry with a rhombic displacement (increasing magnitude of r_{rh}), while the Y direction is symmetric, decreasing r_{cc} and increasing r_{db} . In short, the X displacement moves you towards the S_1/S_0 conical intersection, while the Y displacement moves you from NBD to QC.

Using Fig. S9, it is clear that any dynamics which started in NBD (*i.e.* coming from negative Y along the lower S₁ surface) would almost certainly be split into two separate channels which go towards the two mirror-image copies of the S_1/S_0 conical intersection, and we expect minimal coupling in the dynamics. For clarity, we illustrate this with an example trajectory, drawn as a vector. This conical intersection is also present in the XMS-CASPT2(2,2) method, with almost identical energies and branching plane vectors. Notably, the conical intersection is more peaked, leading to less transfer to the S₂ state.

6 Location of Rydberg states

Table S3: Summary of previous active spaces applied to excited states of this molecule. The nominal active space and basis set are given, with comments on which additional orbitals (all Rydberg) were included over the CASSCF(4,4) method. Coppola *et al.*⁴ also performed some MS- and SS-CASPT2 calculations, and Hernandez *et al.*⁵ some XMS-CASPT2.

Work	Active space	Basis	Differences from (4,4)
Antol ⁶	(4,4)+3s	cc-pVDZ + diffuse S	Additional auxiliary 3s
Valentini <i>et al.</i> ⁷	(4,8)	aug-cc-pVDZ	3s and three 3p
Coppola <i>et al</i> . ⁴	(4,7)	ANO-L-VDZP+1s1p1d	(4,3) with 3s and three 3p
Hernandez <i>et al.</i> ⁵	(4,7)	ANO-S-VDZP	$3s, 3p_x, 3p_y$



Figure S11: SA(8)-CASSCF(4,8)/aug-cc-pVDZ Rydberg states. Left: QC \leftrightarrow S₁/S₀ MECI \leftrightarrow NBD LIIC. The important valence state (referred to as S₁ elsewhere) is far higher in energy, starting as the burgundy state at \approx 7.5 eV above the ground state of NBD. It crosses with the doubly-excited state and moves through the Rydberg manifold (the flat states at \approx 4 eV) before heading to the ground state. Right: S₁/S₀ MECI \leftrightarrow S₁ minimum \leftrightarrow NBD LIIC. Again, the important states start extremely high in energy. On the right half of this pathway, the geometry maintains C_{2v} symmetry, and thus, the singly excited state crosses diabatically with the doubly-excited state. The doubly excited state crosses the Rydberg manifold around the S₁ minimum geometry and then mixes with the singly excited state to move closer to the intersection.

As mentioned in the main text, all previous work on this system has used Rydberg states in the electronic structure. The Rydberg states are generally absent in applications, where the molecules are always in the condensed phase.

When calculating Rydberg states, dynamic correlation is essential. For example, we show SA(8)-CASSCF(4,8)/aug-cc-pVDZ, a non-dynamically correlated method very closely related to those used in previous studies.^{5–7} A brief description of the methods used in those studies is shown in Table S3. The (4,8) active space contains all of the orbitals in the (4,4) active space used in this study *and* additional 3s and three 3p Rydberg orbitals. We use the full aug-cc-pVDZ basis to ensure that all Rydberg states are equally described.

In Fig. S11, one can see that the low-lying valence state (called S₁ elsewhere in this work) is far above the Rydberg manifold, appearing first as the burgundy state at \approx 7.5 eV above the NBD ground state minimum, far away from the correct value should be \approx 5.25 eV. The overall shape of this state is consistent with the CASSCF(4,4) results (*e.g.* in Fig. S13), showing that the description of the valence states is unaffected by the inclusion of the Rydberg states (a fact that also applies to the (2,2) active space). The CASSCF(4,8) thus describes these states as poorly as CASSCF(4,4).

Further, mixed Rydberg/valence systems are not well described by CASSCF. This is because the Rydberg states do not require as much correlation as the valence states, as the Rydberg electron is situated far away from the other electrons. CASSCF, which is not very correlated, therefore describes the Rydberg states better than the valence, which leads to the excitation energies of Rydberg states being *too low*. In this CASSCF(4,8) method, we have a Rydberg manifold which starts at ≈ 5.4 eV above the NBD ground state, lower than its experimental value of closer to 6 eV.¹

The increase in energy of the valence state (caused by the poor description of the (4,4) active space) and the relative decrease in energy of the Rydberg states (by lack of dynamic correlation) causes the Rydberg states to sit far below the valence states, when they should sit far above. Any dynamics on the valence states will have to traverse the Rydberg manifold to reach the conical intersection, leading to extensive coupling into those states and, thus, substantively different dynamics. Finally, we mention that it is also possible to not use diffuse functions in the basis, causing the Rydberg states to artificially rise in energy (perhaps even above the valence states). This is undesirable, as you are deliberately describing one part of the system (the Rydberg states) poorly in order to get a favourable outcome. Additionally, this adds a much larger amount of energy into the system, leading to different dynamics.



Figure S12: Potential energy cuts containing Rydberg states, for CASSCF(2,2) (solid purple) and XMS-CASPT2(4,4) (dashed rose), both using the p-cc-(p)VDZ basis, and XMS-CASPT2(4,8) (green dotted) using the aug-cc-pVDZ basis. Left: QC \leftrightarrow S₁/S₀ MECI \leftrightarrow NBD LIIC. The S₁ valence state (the lowest excited state in NBD) agrees between the (4,4) (without Rydberg) and (4,8) active spaces in XMS-CASPT2, indicating that the Rydberg states do not significantly affect the dynamics. This state is below the Rydberg manifold (the flat set of potentials at \approx 5 eV). Right: S₁/S₀ MECI \leftrightarrow S₁ minimum \leftrightarrow NBD LIIC. Again, the important S₁ state is always below the Rydberg manifold, agreeing well between the (4,4) and (4,8) active spaces.

We can correct these issues by adding correlation. In Figure S12, we show the potential energy surfaces for both LIICs considered in this study for XMS(8)-CASPT2(4,8)/aug-cc-pVDZ, which adds dynamic correlation onto the SA(8)-CASSCF(4,8) method, and compare with CASSCF(2,2) and XMS-CASPT2(4,4). As can be seen, the low-lying S₁ (1 A_2) state agrees well with all methods and is far below the Rydberg manifold, the set of flat states centred at around 6 eV above the NBD minimum. The inclusion of Rydberg states thus does not significantly affect the dynamics on the low-lying S₁ state, as they are well separated in energy in all important geometries, and we can safely remove them from consideration.

Although unsubstituted NBD contains Rydberg states, which are primarily excited in experiments, there is Rydberg-free dynamics upon excitation at < 6 eV. This more closely models the dynamics that would be seen in a practical application, where substituted systems lower the energy of the valence states even further, completely removing all trace

of Rydberg excitation from the system.

7 MRCI

The truncation of CI calculations leads to size-consistency errors, and a multitude of corrections exist to approximate the inclusion of higher excitations.^{8–11} In MRCI calculations with multiple states, these corrections are critical, as the approximate quality of a CI calculation is related to the reference weight c_0 , the coefficient of the wavefunction included to the reference configurations. A helpful analogy is to relate c_0 to the 'amount of work' the MRCI calculation has to perform. A high c_0 indicates that the MRCI calculation has to compensate for less deficiency in the CASSCF wavefunction compared to lower c_0 values. As a consequence, MRCI calculations based on biased active spaces tend to remain biased.

In Fig. S13, we show the CASSCF, MRCI and MRCI+Q results for the QC \leftrightarrow S₁/S₀ MECI \leftrightarrow NBD LIIC for the (2,2) (left) and the (4,4) (right) active space. In the (2,2) active space, the reference weight is relatively constant for all the states, and so the MRCI and MRCI+Q agree closely on the shape of the potential energy surface. We also see that the CASSCF(2,2) results are also fairly close to the MRCI results. On the other hand, the (4,4) active space shows no signs of agreement. This is because the reference weight is much lower for S₁ than the other two states around NBD. This can also be seen in Table S2, where the CASSCF(4,4) S₁ excitation energy is far higher (7.55 eV) than the other methods. As we include dynamic correlation with MRCI, the result improves (to 6.47 eV) but is still not close to the experimental value of 5.25 eV. Only by including the Davidson corrections do we get closer, moving to 5.47 eV (DV3, see later), in acceptable agreement with experiment.



Figure S13: Left: SA(3)-CASSCF (solid, indigo) vs MRCI (dashed, rose) vs MRCI+Q (dotted, green), with both (2,2) (left) and (4,4) right active spaces. All calculations are performed with the p-cc-(p)VDZ basis set. For the (2,2) active space, the MRCI changes the description for S₀ around the NBD minimum, but qualitative agreement is seen elsewhere, even with the Davidson correction. For the (4,4) active space, the three methods do not agree even qualitatively, with a notable $\approx 2 \text{ eV}$ increase in excitation energy in NBD. Notably, the MRCI+Q(4,4) calculations give a similar shape to all three (2,2) active space methods. Calculations not shown for QC, where the (4,4) active space is unstable.

We use the terminology of the COLUMBUS program^{11,12} in defining the size-consistency corrections. For clarity, we repeat them here.

DV1:
$$E_{\text{DV1}} = (1 - c_0^2) E_{\text{corr}}$$
,
DV2: $E_{\text{DV2}} = \frac{(1 - c_0^2)}{c_0^2} E_{\text{corr}}$,
DV3: $E_{\text{DV3}} = \frac{(1 - c_0^2)}{2c_0^2 - 1} E_{\text{corr}}$,
Pople: $E_{\text{Pople}} = \frac{\sqrt{N^2 + 2N\tan^2(2\theta)} - N}{2(\sec(2\theta) - 1)} E_{\text{corr}}$,

where c_0 is the reference weight, $E_{\text{corr}} = E_{\text{MRCI}} - E_{\text{CASSCF}}$, $\theta = \arccos(c_0)$, and *N* is the number of electrons. We compare DV3, DV2, and the Pople correction in Fig. S14. There are no huge deviations in these calculations, and all corrections closely replicate the overall shape of the potentials.



Figure S14: MRCI+Q(4,4) Davidson corrections, calculated using the p-cc-(p)VDZ basis set. The DV3 (solid purple) and Pople (dotted green) corrections agree excellently, while the DV2 slightly deviates, especially on the first excited state of NBD.



Figure S15: Multi-reference formalisms. Potential energy cuts for contracted and uncontracted MRCI schemes, for the QC \leftrightarrow S₁/S₀ MECI \leftrightarrow NBD LIIC. Upper left: uc-MRCI+Q(2,2) (solid purple) and ic-MRCI+Q(2,2) (dashed rose) potentials. Internal contraction makes no difference to the shape of the potential energy surfaces. Upper right: uc-MRCI+Q(4,4) (solid purple) and ic-MRCI+Q(4,4) (dashed rose) potentials. The internal contraction gives different energies from the uncontracted calculations, especially for the states with significant |2ud0⟩ character. Lower right: XMS-CASPT2(2,2) calculations. The contraction has a minimal effect, as seen in the equivalent MRCI calculations. Lower right: XMS-CASPT2(4,4) calculations. A small effect is seen, but here, it affects all states. Geometries are from MRCI(2,2)/p-cc-(p)VDZ LIIC. Calculations with convergence/intruder state issues are not shown. (2,2) CASPT2 calculations use a real shift of 0.2 E_h, (4,4) use 0.4 E_h. All calculations use p-cc-(p)VDZ basis. ucMRCI is performed in COLUMBUS 7.6, SS-SR-XMS-CASPT2 in OpenMolcas v23.2, and icMRCI and MS-MR-XMS-CASPT2 in MOLPRO 2022.2.

The implementation of MRCI in COLUMBUS is 'uncontracted' (ucMRCI), which includes all single and double excitations from each determinant individually. Other MRCI implementations, such as those in ORCA 5.0.4¹³ and Molpro 2022.2¹⁴, use a 'internally contracted' formalism (icMRCI), which only applies the excitation to the entire wavefunction. This leads to fewer variational parameters and, thus, a more approximate wavefunction. The computational saving is often large but is less obvious when dealing with smaller active spaces, as we do here.

In this case, as shown in Fig. S15 (upper two panels), the difference is dependent on the active space. For the (2,2) active space, the uncontracted formalism gives effectively identical curves. For the (4,4) active space, the difference is much larger. Interestingly, this difference is specific to the second state, only affecting the state with large $|2ud0\rangle$ character around NBD. This might be rationalised as a consequence of the poor description of the second state - the icMRCI method, which excites from the reference wavefunction, does not have the full flexibility needed to describe the final state. The (2,2) active space, which gives a more equal description of the state, gives little qualitative different between the two contraction schemes.

It should be noted that a similar problem exists in CASPT2. The split is between the 'multi-state multi-reference' (MS-MR), referring to a formalism which calculates all states together, and 'single-state single-reference' (SS-SR), a formalism which combines all of the states separately after calculation (which decreases computational time). Previous work has shown that these approximations are less important than they are in MRCI.¹⁵ We show the results for the different approximations in Fig. S15 (lower panels). In XMS-CASPT2(2,2), the effect of contraction has a far less obvious effect, while there is at least a small difference in XMS-CASPT2(4,4), in line with the results of MRCI. The SS-SR calculations come from the OpenMolcas program (as used throughout), while the MS-MR calculations come from Molpro. As the imaginary shift used previously is not implemented in Molpro, a real shift is used (0.2 E_h for the (2,2) active space, 0.4 E_h for the (4,4)). The real shift is known to cause its own issues with intruder states, and this is seen around the ground state minimum of QC, which is not shown on the figure.

8 SHCI and LR-CCSD

In the main text, we compare our multi-configurational methods with LR-CC3, a very high-level method for calculating excitation energies from a coupled-cluster wavefunction. Here, we show two more non-active space methods: SHCI, which is a variant of selected configuration interaction, and LR-CCSD, which which calculates the excitation energies from a CCSD ground state.

Selected configuration interaction (CI) methods approximate full CI by attempting to include only important configurations in the expansion. Unlike traditional truncated CI, such as CISD, they do limit the degree of excitation, but rather include configurations based on an importance criterion, effectively ignoring determinants that do not contribute significantly. The most important advantage is their lack of human bias; they do not require the selection of an active space and generally provide a comparatively even-handed description of all electronic states considered. While many flavours of selected CI exist, we use heat-bath CI (HCI),¹⁶ which is known to be computationally efficient. We perform the calculations in a large active space that consists of 20 electrons in 80 orbitals since all-electron calculations are not feasible. This active space is chosen to ensure that all low-energy orbitals are included. Furthermore, the contribution from determinants not selected is estimated using a stochastic perturbation theory.¹⁶

We only calculate the ground and first excited ($|2ud0\rangle$) states using SHCI. As seen in Fig. S16, the SHCI results agree well with MRCI+Q(4,4), confirming that the active space procedure is reasonably unbiased. It is worth noting that as well as providing an unbiased



Figure S16: SHCI(2,2) (solid, purple) vs XMS-CASPT2(2,2) (dashed, rose) vs MRCI+Q(4,4) (dotted, green) calculations, all for p-cc-(p)VDZ basis. The agreement is strong across all geometries, with only a small deviation in excitation energies. All calculations on MRCI geometries (see Methods).

reference, the selected CI methods are also interesting candidates for 'black-box' electronic structure methods for dynamics, with a good mixture of static and dynamic correlation and relatively straightforward gradient and non-adiabatic coupling implementations.¹⁷ Currently, their usage is limited by their computational costs, but ongoing improvements in theory and algorithms could make them ubiquitous.

Finally, we show LR-CCSD.^{18,19} Unfortunately, LR-CCSD is limited to only describing singly-excited states well — this system, which contains important doubly-excited states, is not well described by it. This can be seen in Fig. S17, which shows the LR-CCSD with a notably steep gradient around the intersection in both LIICs. Other single-reference correlated excited state methods (e.g. ADC(2) and CC2) only give worse results, as the double excitation crucial to the description is included at an even lower level, if at all.



Figure S17: Potential energy cuts for LR-CCSD, contrasted against the CASSCF(2,2) and XMS-CASPT2(4,4). Left: QC \leftrightarrow S₁/S₀ MECI \leftrightarrow NBD LIIC. The LR-CCSD agrees very well with the CASSCF(2,2), but shows a slightly different shape to the XMS-CASPT2(4,4) on the excited state. Notably, the gradients around the MECI are slightly too steep. Right: S₁/S₀ MECI \leftrightarrow S₁ minimum \leftrightarrow NBD LIIC. Again, the LR-CCSD agrees fairly well with CASSCF(2,2) and XMS-CASPT2(4,4).

As a final check, we show the LR-CCSD calculations performed with our p-cc-(p)VDZ basis and the larger aug-cc-pVTZ basis in Fig. S18. We do this primarily to show that our new contraction, p-cc-(p)VDZ, is close to convergence, as coupled cluster methods are notorious for needing large basis sets to get good agreement. The shape of the potentials is consistent between the two methods, implying that our basis is appropriate. These calculations were not feasible for LR-CC3, but we assume the trend is approximately continued, and we can trust that the current potentials are close to correct.



Figure S18: Basis sets for LR-CCSD, using the S_1/S_0 MECI $\leftrightarrow S_1$ minimum \leftrightarrow NBD LIIC, the overall agreement between the p-cc-(p)VDZ and aug-cc-pVTZ basis sets is good, indicating that the p-cc-(p)VDZ is at least somewhat converged.

8.1 Computational details for SHCI

Stochastic heat bath configuration interaction (SHCI) calculates were performed using the PySCF²⁰/DICE^{16,21–23} interface. The SHCI used the pseudo-canonical orbitals from SA(3)-CASSCF(2,2) calculations to ensure that orbitals are smooth along the LIICs, and then performs the SHCI within a (20,80) active space. Expanding the active space is not computationally feasible for the entire pathways but gave similar relative energy gaps at test points. The variational portion was converged to $\epsilon_1 = 10^{-4}$, and the stochastic perturbative correction used 30 samples of 200 variationally chosen configurations, with $\epsilon_2 = 10^{-7}$. The stochastic portion gave errors of less than 5×10^{-4} E_h ≈ 0.01 eV, which suffices for comparison — note, this is *not* the error with respect to FCI, but the error in the stochastic sampling. SHCI calculations for the QC \leftrightarrow S₁/S₀ MECI \leftrightarrow NBD were performed simultaneously for three states, with the second (triplet) solution discarded, while calculations for the S₁/S₀ MECI \leftrightarrow S₁ min. \leftrightarrow NBD were performed with time-reversal symmetry to remove the triplet state.

9 Other multi-reference methods

There are many ways to add correlation to a CASSCF calculation. We utilised MRCI and XMS-CASPT2, but here we show additional calculations performed using MS-CASPT2, QD-NEVPT2 and XMC-QDPT2 (three different flavours of quasi-degenerate multi-reference perturbation theory). We compare it to XMS-CASPT2(2,2), which gave good agreement to the MRCI+Q(4,4) calculations. The vertical excitation values are shown in Table S2, where QD-NEVPT2 and XMC-QDPT2 show very similar values to XMS-CASPT2 with the (2,2) active space. MS-CASPT2, on the other hand, shows a remarkably low S₁ vertical excitation energy of 4.85 eV. These trends are continued in Fig. S19, with QD-NEVPT2 and XMC-QDPT2 both showing exceptional agreement. MS-CASPT2, on the other hand, is remarkably lower across the potential. Similar values are also seen in the results of

Coppola *et al.*,⁴ as well as our own previous work.²⁴ We noticed that the agreement of MS-CASPT2 improved when including the IPEA shift with its standard value of 0.25 E_h .

All calculations in Fig. S19 use the p-cc-(p)VDZ basis and the (2,2) active space. The QD-FIC-NEVPT2 calculations were performed using the ORCA 5.0.4 program.¹³ XMC-QDPT2(2,2) calculations were performed in Firefly.²⁵ Some minor deviations are seen around the NBD, but this is likely to do with both the different implementations of the level-shift (0.2*i* in XMS-CASPT2 vs. ISA=0.02 in XMC-QDPT2). MS-CASPT2 calculations were performed in OpenMolcas.²⁶



Figure S19: Potential energy curves for XMS-CASPT2 (purple solid), MS-CASPT2 (rose dashed), QD-NEVPT2 (green dotted), XMC-QDPT2 (sand dashdot lines), all based on a SA(3)-CASSCF(2,2)/p-cc-(p)VDZ reference. The QD-NEVPT2, XMC-QDPT2 and XMS-CASPT2 agree well, with only a small and roughly constant energy difference between the two curves. The MS-CASPT2, on the other hand, seems to get the overall shape of the potential energy surface wrong, at least compared to XMS-CASPT2, which compares favourably with the MRCI+Q(4,4).

Finally, in Fig. S20, we show the potential energy cuts using different values of the imaginary shift. Clearly, the value of the shift affects the energy of the S_2 state around the NBD minimum (vertical excitation energies can be found in Table S2). In general, a lower shift gives a lower excitation energy of S_2 . Unfortunately, upon using a 0.1*i* shift, we found minor issues with intruder states. Therefore, we use 0.2*i* for the rest of the work as an acceptable compromise between accuracy and stability.



Figure S20: Potential energy cuts for XMS-CASPT2(2,2) with different shift values, all using p-cc-(p)VDZ basis. As the shift decreases, the slope of the doubly excited $S_2 |2020\rangle$ state around NBD gets slightly shifted. All calculations in the text use a value of 0.2i.

10 Basis sets

For clarity, we include a table of the basis set primitives and contractions in Table S4. The validity of this basis set can be seen by comparison to the ANO-L-VQZP basis. The ANO-L basis has a particularly large set of primitive functions, and the truncation at quadruple-zeta-plus-polarisation leads to fantastic energies and properties. A similar effect can be seen in the earlier comparison for LR-CCSD, shown in Fig. S18 and the associated discussion.

First, we can look at the potential energy surfaces in both CASSCF and XMS-CASPT2 in Fig. S21. The potential cuts show excellent agreement between the two methods, especially in the correlated XMS-CASPT2 calculations. Furthermore, we show the conical intersection parameters shown in Table S5, which mimics Table 2 in the main text. The basis set change gives minor changes to both the structure and the potential energy surface around the intersection, but overall the methods are well converged. Finally, the structures of the ground state minima (see Table S1) show close agreement, and further good agreement to a previous study using large basis sets MP2 calculations.

The primary difference between the descriptions for different basis sets is caused by the diffuse nature of the states, which is evident from the radial second moment of the charge for each state, given as $\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$. Here, the integration is performed over both the electrons and the nuclei to cancel out effects due to the geometry change. In Fig. S22, the diffuseness, which increases going up the *y*-axis, for the two excited states can be seen to increase significantly around the QC ground state minimum. Here, the orbital characters change such that the B₁ (see Fig. S1) orbital gains considerable Rydberg character. S₂, which is a state of |2200⟩ character, is therefore even more diffuse. A smaller (but similar) effect can be seen around the NBD minimum. Incorrectly dealing with this diffuseness (*e.g.* by using an insufficiently diffuse basis) leads to a severe overestimation of excitation energies into these states, as seen in Fig. S21.

Table S4: Primitives and contractions for the p-cc-(p)VDZ basis set. This is a effectively a pruned aug-cc-pVDZ basis set, removing all diffuse and polarisation functions off of hydrogen atoms (a [4s|2p] contraction), and the S and D angular momentum diffuse functions off of carbon atoms (a [9s5p1d|3s3p1d] contraction). Zero values are not shown.

Atom	Ang. mom.	Primitives	Contractions		
Η	S	13.01	0.019685		
		1.962	0.137977		
		0.4446	0.478148		
		0.122	0.50124	1	
С	S	6665	0.000692	-0.000146	
		1000	0.005329	-0.001154	
		228	0.027077	-0.005725	
		64.71	0.101718	-0.023312	
		21.06	0.27474	-0.063955	
		7.495	0.448564	-0.149981	
		2.797	0.285074	-0.127262	
		0.5215	0.015204	0.544529	
		0.1596	-0.003191	0.580496	1
	Р	9.439	0.038109		
		2.002	0.20948		
		0.5456	0.508557		
		0.1517	0.468842	1	
		0.04041			1
	D	0.55	1		



Figure S21: Potential energy cuts calculated using p-cc-(p)VDZ basis (solid rose) vs ANO-L-VQZP (dashed green) for SA(3)-CASSCF(2,2) (left) and XMS-CASPT2 (right). CASSCF calculations performed on CASSCF geometries, and CASPT2 calculations on MRCI geometries.

Table S5: Conical intersection parameters. *P* and *B* parameters and carbon-carbon distances (in Ångströms for optimised S_1/S_0 MECI for the (2,2) active space for SA(3)-CASSCF, XMS-CASPT2 (with 0.2*i* shift), for the p-cc-(p)VDZ and ANO-L-VTZp basis set (ANO-L-VTZP on the carbons and ANO-L-VTZ on the hydrogens). The conical intersections all have a C_2 optimised geometry.

Basis set	Method	Р	В	r _{cc}	r _{db}	r _{rh}
p-cc-(p)VDZ	CASSCF	0.789	0.857	1.943	1.443	0.499
	XMS-CASPT2	0.560	1.168	2.011	1.490	0.555
ANO-L-VTZ(p)	CASSCF	0.768	0.834	1.937	1.435	0.484
	XMS-CASPT2	0.511	1.082	1.996	1.474	0.530



Figure S22: $-\langle r^2 \rangle$ for three analysed states SA(3)-CASSCF(2,2)/p-cc-(p)VDZ calculations. Values increasing indicate increasing electronic diffuseness. The $\langle r^2 \rangle$ values significantly increase for the two excited states around the QC ground state minimum. At the conical intersection, the states change character, leading to discontinuities in the curves.

11 Nature of the potential energy surfaces



Figure S23: Annotated potential energy cut for the QC \leftrightarrow S₁/S₀ MECI \leftrightarrow NBD LIIC using XMS-CASPT2(2,2). The character labels use the orbital labelling from Fig. 2 (main text) and S1. Close to the intersection, S₁ gains double excitation character. All other methods except CASSCF(4,4) show good agreement in the character of the states.

In Fig. S23, we show the XMS-CASPT2(2,2) potential energy surfaces with labels of approximate character. All other methods studied *except* CASSCF(4,4) show very similar characters. Near the conical intersection, S_1 and S_2 become mixed in character, with S_1 gaining double excitation character, with the region very close involving all three important configurations.



Figure S24: Fraction of single excitations (T1) for the S_1 LR-CC3 and LR-CCSD wavefunctions. Left: QC $\leftrightarrow S_1/S_0$ MECI \leftrightarrow NBD LIIC. The singly-excited character drops around the conical intersection, but much more noticeably for LR-CC3 than LR-CCSD. This spike at the conical intersection indicates the poor description. Right: S_1/S_0 MECI $\leftrightarrow S_1$ minimum \leftrightarrow NBD LIIC. Again, the doubly-excited character is highest at the conical intersection. Points not shown for the S_1/S_0 MECI, as the LR-CC wavefunction shows convergence issues.

As mentioned, the S_1 state gains double excitation character around the S_1/S_0 conical intersection. We use the fraction of single excitations (T1), the sum of all singly-excited amplitudes. Lower values indicate more doubly-excited character.^{27,28}. This provides a good estimate of the doubly-excited character of the system. We show this using LR-CC3 and LR-CCSD S_1 states, shown in Fig. S24. As is clear, the doubly-excited character is very high around conical intersection. Notably, the LR-CCSD values are higher than the LR-CC3 values, in accordance with the poor description seen in Section 8. More approximate methods, such as LR-CC2 and ADC(2), would give even worse descriptions.



Figure S25: Potential energy cuts for the (2,2) (purple solid) and (4,3) (rose dashed) active space for the QC \leftrightarrow S₁/S₀ MECI \leftrightarrow NBD LIIC. Left: CASSCF. Right: XMS-CASPT2. The agreement is strong across the pathway, except for presence of the 1¹B₂ in the (4,3) active state. For dynamics on the lower 1¹A₂ (S₁) state, this state is not important.

12 Summary of Calculations

Table S6: Summary of methods evaluated in this study. In order, the columns indicated: the active space, whether they are stable in the QC geometry, whether they can be used in a dynamics simulation, whether their S_1/S_0 CI has bifurcating character and whether they show a local minimum on the S_1 surface. N/A indicates that the calculation has not been performed.

Method	(<i>m</i> , <i>n</i>)	Stable in QC?	Dynamics?	Bifurcating?	S ₁ min.?
CASSCF	(2,2)	Yes	Yes	Yes	Yes
	(4,4)	No	Yes	Yes	Yes
XMS-CASPT2	(2,2)	Yes	Yes	No	No
	(4,4)	No	Yes	Yes	Yes
MRCI	(2,2)	Yes	Yes	No	Yes
	(4,4)	No	Yes	Yes	No
MRCI+Q	(2,2)	Yes	No	N/A	Yes
	(4,4)	No	No	N/A	Yes
LR-CC3	HF	Yes	No	N/A	Yes
LR-CCSD	HF	Yes	No	N/A	Yes
SHCI	(20,80)	Yes	Yes	N/A	Yes

13 CASSCF(4,3)

In addition to the CASSCF(2,2) and CASSCF(4,4), there exists an alternative choice: CASSCF(4,3). Using the nomenclature of Fig. 2 (and Fig. S1), this includes the A_1 , B_1 , and B_2 orbitals. In addition, we state average over four states, giving SA(4)-CASSCF(4,3), adding an additional valence state: the 1^1B_2 state, which can be observed spectroscopically above the 1^1A_2 state^{1,29}.

All of the critical geometries in this paper have at least C_2 symmetry, with some being in the C_{2v} sub-group, and all states considered belong to the A irreducible representation (irrep). When adding the A_1 orbital to form the (4,3) active space, we only add one additional configuration in the A irrep, namely the $|0220\rangle$ configuration. In C_{2v} geometries, this is A_1 and contributes to the two A_1 states S_0 and S_2 , primarily the latter. This does not significantly affect to the wavefunction, and the presence of the A_1 orbital can lead to instability around QC geometries, where it lowers significantly in energy.

As such, the CASSCF excitation energies (Table S2), optimised geometries (Table S1) and overall potential energy surfaces (Fig. S25, left panel) are incredibly similar between the methods, as well as the qualitative features of the potential. The XMS-CASPT2 results, shown as above, share the same similarity. We also mention, finally, that as the CASSCF(4,3) wavefunction is state-averaged over four states, the two states studied here, S₀ and S₁, have a lower weight in the wavefunction, which may negatively affect their description.

However, this symmetry-based analysis is only valid within symmetric geometries of the unsubstituted (or symmetrically substituted) variants of the QC/NBD system. It is plausible that the additional orbitals could lead to better results in asymmetrically substituted variants or non-symmetric geometries, where contribution of the additional orbital is no longer symmetry forbidden. In addition, the (4,3) allows for the calculation of the $1^{1}B_{2}$ state, which could be useful for ultrafast experiments with excitation energies of ≈ 6 eV.

С	-0.00623762	0.00112809	-0.01783509
С	2.46952702	0.00113714	-0.01782721
С	-0.00623241	0.00112590	-1.34758024
С	2.46953222	0.00113360	-1.34756813
С	1.23163817	0.79689777	0.43333960
С	1.23165004	0.79689305	-1.79874838
С	1.23164036	1.87320553	-0.68270700
Η	-0.69996623	-0.50029786	0.64449358
Η	3.16324837	-0.50028992	0.64450757
Η	-0.69995108	-0.50030785	-2.00991290
Η	3.16326333	-0.50029138	-2.00989473
Η	1.23163506	1.13729348	1.46891791
Η	1.23165407	1.13728394	-2.83432830
Η	0.33495108	2.49860759	-0.68271213
Η	2.12832761	2.49861092	-0.68270456

14 Important geometries

Table S7: NBD S₀ geometry optimised at CASSCF(2,2)/p-cc-(p)VDZ level. Distances in Ångströms

С	-0.01145559	0.01158941	-0.01135907
С	1.53739527	0.01158779	-0.01135237
С	-0.01145467	0.01155994	-1.54175823
С	1.53740665	0.01158450	-1.54174779
С	0.76297273	1.25126614	0.36989437
С	0.76295163	1.25123727	-1.92302270
С	0.76296521	2.24291674	-0.77657493
Η	-0.71360035	-0.49523713	0.63679114
Η	2.23950681	-0.49526863	0.63680775
Η	-0.71360322	-0.49528638	-2.18989435
Η	2.23952093	-0.49528504	-2.18988826
Η	0.76297739	1.57342865	1.40570641
Η	0.76297060	1.57337379	-2.95884322
Η	-0.12694439	2.88241733	-0.77657997
Η	1.65289101	2.88239562	-0.77659876

Table S8: QC S $_0$ geometry optimised at CASSCF(2,2)/p-cc-(p)VDZ level. Distances in Ångströms

С	0.06659730	-0.02880259	-0.02563437
С	2.00952085	0.00421747	-0.01385623
С	0.38714943	0.00324735	-1.43196211
С	2.31906961	0.21014800	-1.40784916
С	1.07367793	1.00658507	0.49581788
С	1.18685157	1.17562053	-1.78739361
С	1.06672984	2.10636002	-0.57377451
Η	-0.20016431	-0.93137068	0.50395810
Η	2.41088169	-0.78642470	0.60695968
Η	0.08153018	-0.73587112	-2.16128877
Η	2.69126986	-0.56875204	-2.05671580
Η	1.05710172	1.25334693	1.55126345
Η	1.16341457	1.56844681	-2.79747720
Η	0.13354623	2.67323379	-0.55901404
Η	1.92221352	2.78102518	-0.50047330

Table S9: S_1/S_0 MECI geometry optimised at CASSCF(2,2)/p-cc-(p)VDZ level. Distances in Ångströms

С	0.17298688	-0.02618520	0.02288223
С	2.29030187	-0.02617869	0.02289329
С	0.17299268	-0.02618849	-1.38829861
С	2.29030760	-0.02618168	-1.38828755
С	1.23163931	0.95165983	0.45363687
С	1.23164898	0.95165483	-1.81904650
С	1.23164094	1.99160838	-0.68270709
Η	-0.35088109	-0.71008531	0.67492913
Η	2.81416716	-0.71007700	0.67494457
Η	-0.35086835	-0.71009296	-2.04034685
Η	2.81417978	-0.71008144	-2.04033145
Η	1.23163367	1.28026360	1.48865171
Η	1.23165256	1.28025404	-2.85406278
Η	0.33518152	2.61587726	-0.68271194
Η	2.12809647	2.61588283	-0.68270504

Table S10: S1 minimum geometry optimised at CASSCF(2,2)/p-cc-(p)VDZ level. Distances in Ångströms

С	-0.005267	0.005148	-0.013416
С	2.468636	0.005136	-0.013417
С	-0.005319	0.005169	-1.351998
С	2.468705	0.005157	-1.351966
С	1.231578	0.801709	0.436135
С	1.231592	0.801714	-1.801534
С	1.231671	1.877629	-0.682714
Η	-0.698233	-0.503522	0.654364
Η	3.161583	-0.503609	0.654335
Η	-0.698269	-0.503486	-2.019780
Η	3.161652	-0.503574	-2.019704
Η	1.231427	1.145650	1.476688
Η	1.231455	1.145545	-2.842151
Η	0.328863	2.504368	-0.682730
Η	2.134465	2.504341	-0.682718

Table S11: NBD S₀ geometry optimised at MRCI(2,2)/p-cc-(p)VDZ level. Distances in Ångströms

С	-0.003622	0.010827	-0.007716
С	1.531534	0.011746	-0.007673
С	-0.003609	0.010794	-1.545401
С	1.531543	0.011762	-1.545406
С	0.763251	1.261201	0.371409
С	0.763256	1.261178	-1.924555
С	0.762701	2.249651	-0.776582
Η	-0.702141	-0.506174	0.646330
Η	2.231175	-0.504045	0.646067
Η	-0.702286	-0.506115	-2.199341
Η	2.231015	-0.504158	-2.199235
Η	0.762730	1.583453	1.412934
Η	0.763126	1.583402	-2.966090
Η	-0.133219	2.890123	-0.776586
Η	1.657823	2.891231	-0.776592

Table S12: QC S₀ geometry optimised at MRCI(2,2)/p-cc-(p)VDZ level. Distances in Ångströms

С	0.057015	-0.020780	-0.030176
С	2.011637	0.010059	0.000095
С	0.383132	0.010877	-1.445441
С	2.326778	0.218583	-1.402547
С	1.055737	1.013460	0.496668
С	1.202942	1.184792	-1.787452
С	1.065984	2.112571	-0.573453
Η	-0.204369	-0.930047	0.503658
Η	2.412487	-0.784986	0.627622
Η	0.078165	-0.731305	-2.182146
Η	2.694483	-0.566871	-2.056722
Η	1.029029	1.267554	1.556603
Η	1.188653	1.586820	-2.800812
Η	0.127634	2.683228	-0.573734
Η	1.926344	2.789366	-0.484636

Table S13: S_1/S_0 MECI geometry optimised at MRCI(2,2)/p-cc-(p)VDZ level. Distances in Ångströms

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