

Supplementary Material

**“Charge Migration In Polycyclic Norbornadiene Cations:
Winning The Race Against Decoherence”**

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S1 Geometries

S1.1 Norbornadiene - Minimum

Table S1: Equilibrium geometry of neutral norbornadiene as computed with B3LYP/6-31G*

	Cartesian Coordinates (Å)		
C	1.245504	0.667947	-0.520644
C	0.000000	1.122691	0.271521
C	-1.245504	0.667947	-0.520644
C	-1.245504	-0.667947	-0.520644
C	0.000000	-1.122691	0.271521
C	1.245504	-0.667947	-0.520644
H	1.936233	1.339433	-1.018889
H	-1.936233	1.339433	-1.018889
H	-1.936233	-1.339433	-1.018889
H	1.936233	-1.339433	-1.018889
C	0.000000	0.000000	1.355150
H	0.900255	0.000000	1.978744
H	-0.900255	0.000000	1.978744
H	0.000000	2.160206	0.612191
H	0.000000	-2.160206	0.612191

S1.2 Norbornadiene - Conical Intersection

Geometry of norbornadiene at which the conical intersection exists:

Table S2: Geometry of norbornadiene cation at which the conical intersection between states 1 and 2 exists, as found using CAS(3,4) (see main text)

	Cartesian Coordinates (Å)		
C	1.270634	0.682297	-0.521783
C	0.000000	1.162674	0.113433
C	-1.270634	0.682297	-0.521783
C	-1.270634	-0.682297	-0.521783
C	0.000000	-1.162674	0.113433
C	1.270634	-0.682297	-0.521783
H	2.093691	1.326350	-0.762202
H	-2.093691	1.326350	-0.762202
H	-2.093691	-1.326350	-0.762202
H	2.093691	-1.326350	-0.762202
C	0.000000	0.000000	1.256456
H	0.883139	0.000000	1.867865
H	-0.883139	0.000000	1.867865
H	0.000000	2.196063	0.419409
H	0.000000	-2.196063	0.419409

S1.3 PLN2

Table S3: Equilibrium geometry of neutral PLN2 as computed with B3LYP/6-31G*

	Cartesian Coordinates (Å)		
C	-0.670312	2.411182	-0.768780
C	-1.129296	1.375050	0.262835
C	-0.787867	-0.000193	-0.418513
C	0.787867	0.000193	-0.418513
C	1.129296	1.375467	0.262473
C	0.669936	2.411750	-0.768624
H	-2.160048	-1.472274	0.614726
H	-1.330601	2.947328	-1.443714
H	-2.159982	1.471735	0.615328
C	-1.129296	-1.375467	0.262473
C	1.129296	-1.375050	0.262835
H	2.160048	1.472274	0.614726
H	1.329901	2.948380	-1.443491
C	0.670312	-2.411182	-0.768780
C	-0.669936	-2.411750	-0.768624
H	2.159982	-1.471735	0.615328
H	1.330601	-2.947328	-1.443714
H	-1.329901	-2.948380	-1.443491
C	0.000215	1.574432	1.304010
C	-0.000215	-1.574432	1.304010
H	0.000100	-2.591707	1.707409
H	-0.000973	-0.874670	2.137881
H	0.000973	0.874670	2.137881
H	-0.000100	2.591707	1.707409
H	-1.207975	0.000015	-1.428543
H	1.207975	-0.000015	-1.428543

S1.4 PLN3

Table S4: Equilibrium geometry of neutral PLN3 as computed with B3LYP/6-31G*

	Cartesian Coordinates (Å)		
C	0.670603	-1.102181	3.531019
C	1.129889	0.101404	2.704950
C	0.790247	-0.323748	1.226818
C	-0.790221	-0.323809	1.226819
C	-1.129895	0.101319	2.704951
C	-0.670519	-1.102229	3.531025
H	1.329629	-1.868344	3.928294
H	2.160550	0.430283	2.863763
H	1.208081	-1.321829	1.060797
H	-1.207979	-1.321923	1.060800
H	-1.329487	-1.868438	3.928303
C	-0.000041	1.086322	3.094826
H	-0.000077	2.040190	2.570450
H	-0.000047	1.286700	4.170772
C	-1.136838	0.577301	0.000000
C	-0.790221	-0.323809	-1.226819
C	0.790247	-0.323748	-1.226818
C	1.136792	0.577391	0.000000
C	-0.000065	1.621143	0.000000
H	-0.000090	2.275516	0.867873
H	-0.000090	2.275516	-0.867873
H	-2.160397	0.967671	0.000000
H	1.208081	-1.321829	-1.060797
H	2.160320	0.967841	0.000000
C	-1.129895	0.101319	-2.704951
C	-0.670519	-1.102229	-3.531025
C	0.670603	-1.102181	-3.531019
C	1.129889	0.101404	-2.704950
C	-0.000041	1.086322	-3.094826
H	-0.000077	2.040190	-2.570450
H	-0.000047	1.286700	-4.170772
H	2.160550	0.430283	-2.863763
H	-2.160582	0.430121	-2.863764
H	-1.329487	-1.868438	-3.928303
H	1.329629	6 -1.868344	-3.928294
H	-1.207979	-1.321923	-1.060800
H	-2.160582	0.430121	2.863764

S2 Energy Gap

Table S5: Energy gaps (ΔE) between cationic states at the neutral equilibrium geometries, calculated using CASSCF(3,4)/6-31G*, and the distance between π bonds

	1-Ring	2-Ring	3-Ring	4-ring	5-ring
R [Å]	2.49	4.72	7.06	9.07	10.75
ΔE	1.15	0.98	0.27	0.09	0.03

The energy gap can be rationalized using Valence Bond (VB) theory. If we have localized π_a and π_b orbitals localized on the two ‘ends’ of the molecule, two configurations can be constructed where one of the two π orbitals is singly occupied and the other is doubly occupied:

$$\text{Configuration 1: } |(core)\pi_a^2\pi_b^1\rangle \quad (\text{S1})$$

$$\text{Configuration 2: } |(core)\pi_a^1\pi_b^2\rangle \quad (\text{S2})$$

The VB Hamiltonian in the space of the two configurations:

$$\mathbf{H} = \begin{pmatrix} Q & K \\ K & Q \end{pmatrix}$$

$$Q = \langle ab|H|ab\rangle = \langle a|h|a\rangle + \langle b|h|b\rangle + \langle ab|g|ab\rangle \quad (\text{S3})$$

$$K = \langle ab|H|ba\rangle = \langle ab|g|ba\rangle + 2S_{ab}\langle a|h|b\rangle \quad (\text{S4})$$

where a and b are orbitals, S_{ab} is their overlap, h is the one-electron kinetic plus electron attraction operator, and g is the electron-electron repulsion.

Giving the energies:

$$E_0 = Q + K \quad (\text{S5})$$

$$E_1 = Q - K \quad (\text{S6})$$

$$\Delta E = 2K \quad (\text{S7})$$

It has been shown that K has a simple behaviour with R, showing an approximate exponential decay of the energy gap¹. This behaviour accounts for the energy gap trend for the PLN systems (table S2 and shown graphically in figure 3 in main text).

¹F. Bernardi, M. Olivucci, and M. A. Robb, J. Am. Chem. Soc. 114, 1606 (1992).

S3 Gradient Differences

The gradient differences reported in the main text were calculated using CAS(3,4)/6-31G* for the 1- and 2-ring systems. Due to computational expense, a smaller basis set (STO-3G) was used in the computation of the gradient difference for the 3-ring system.

The trend in the magnitude of the gradient difference is of key importance. Here we show the reporting of the 3-ring value computed with a different basis set is valid, as the STO-3G values show not only the same trend as the 6-31G* ones, but also give the same numerical values.

Table S6: Magnitude of the gradient difference between cationic states at the neutral equilibrium geometries, calculated using CASSCF(3,4) with different basis sets

	1-Ring	2-Ring	3-Ring
Δg :			
STO-3G	0.08	0.05	0.02
6-31G*	0.08	0.05	-

S4 Dipole Moment

Although our analysis is mainly in terms of the spin density, for the fixed nuclei simulations we can equally study the dipole moment. To illustrate this, we take the fixed nuclei simulation after ionization of norbornadiene (spin density oscillation shown in main text figure 2) and analyse in terms of the dipole moment along the molecular (z) axis:



The result of this analysis is shown in figure S1. This shows the positive charge oscillating from one end of the molecule to the other, to sites equi-distant from the centre of mass, i.e. between ethylenic moieties, with a frequency in agreement with the spin density analysis.

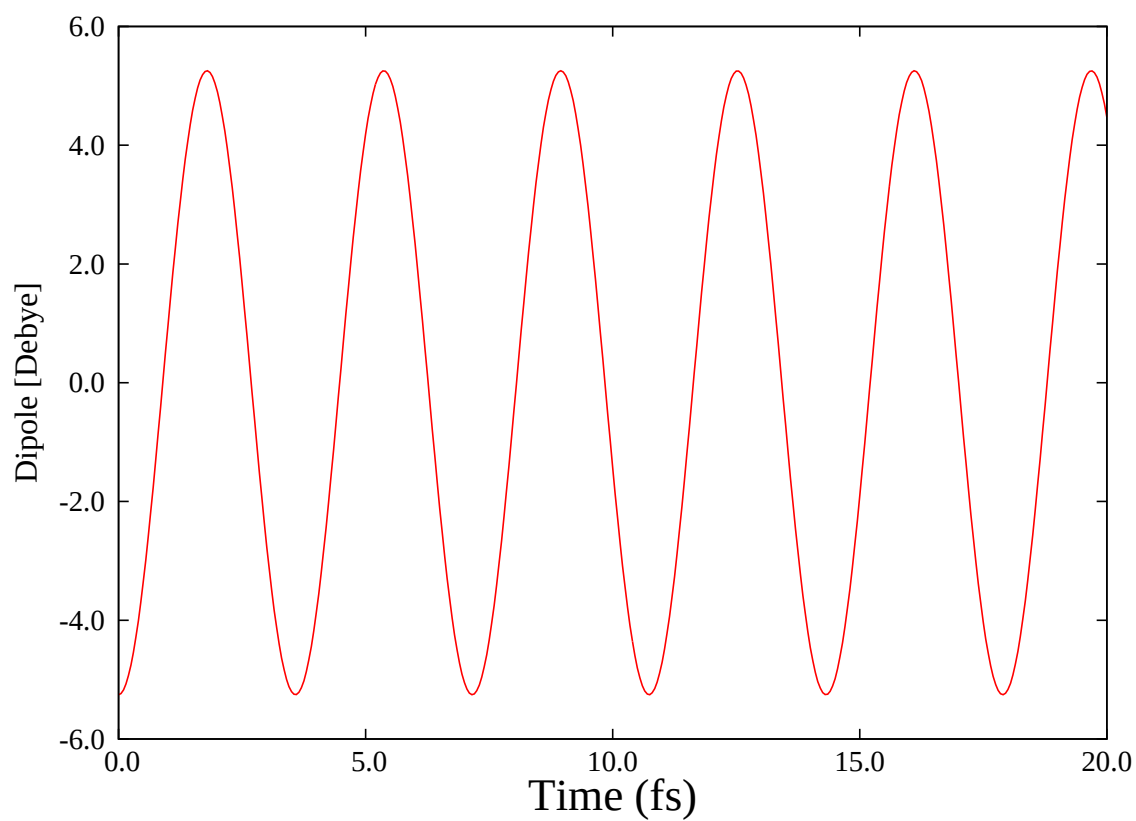


Figure S1: Time evolution of the dipole moment along the molecular axis upon ionization at the neutral equilibrium geometry of norbornadiene, creating a superposition of the lowest two electronic states.

S5 Dephasing

When dephasing occurs the average spin density is delocalized between sites, this is shown in figure S2, where the average spin density on both bonds is given

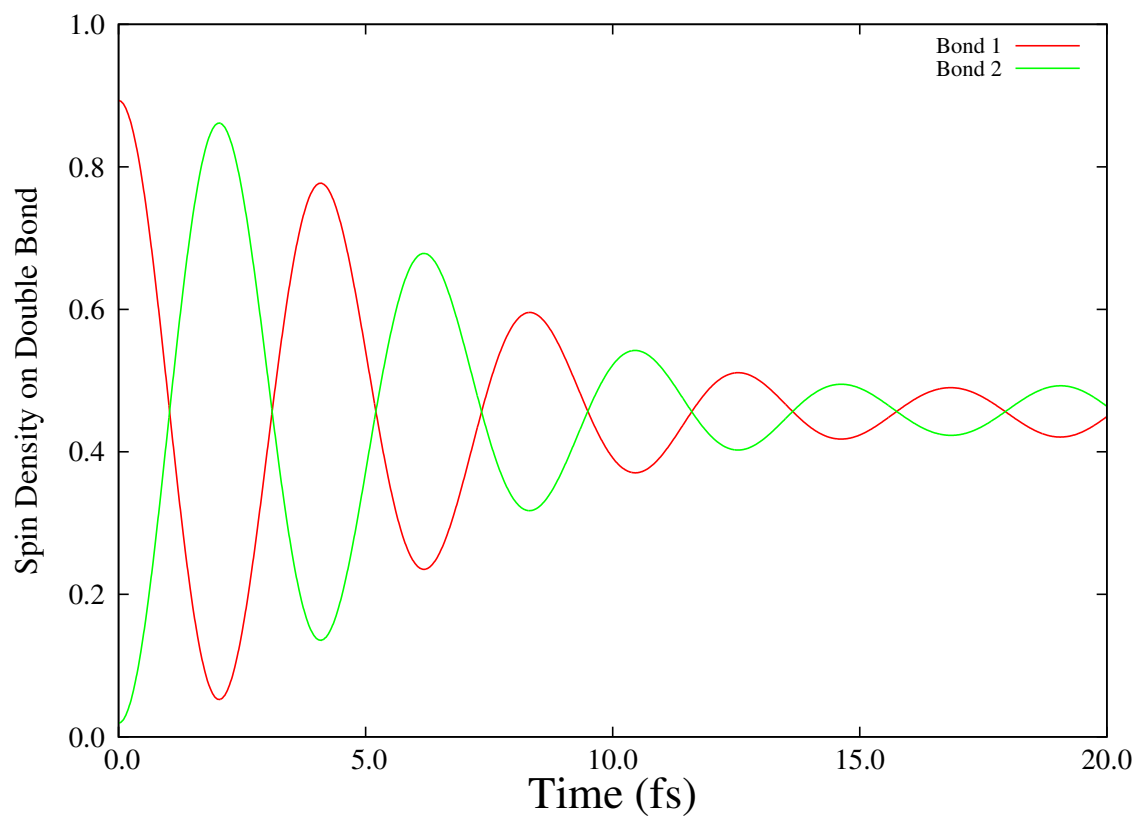


Figure S2: PLN2 average spin density on both bonds from 500 fixed nuclei simulations