

## SUPPLEMENTARY MATERIAL

### Contents:

**SM1. Synthesis of quadricyclane.**

**SM2. The GIAO calculated  $^1\text{H}$  and  $^{13}\text{C}$  magnetic shielding and spin-spin coupling constants.**

**SM3. Fits to the lowest two ionization energies for norbornadiene and quadricyclane and the combined 3rd state of QC.**

**SM4. Comparison of the molecular structures of NBD and QC with experimental microwave and other spectral data.**

**SM5. The ground state equilibrium structures of NBD and QC.**

**SM6. Vibration frequencies of the ground and ionic states.**

**SM7. Bond and ring critical points.**

**SM1. Synthesis of quadricyclane.**

This was prepared using a published procedure.<sup>1</sup> Irradiation of a solution of freshly redistilled norbornadiene (19.5 g, 0.21 mmol) in diethyl ether (500 mL) containing acetophenone (0.9 g) as photosensitizer,<sup>2</sup> using a water-cooled 400 W medium-pressure mercury discharge lamp. After 24 h the ether was removed from the solution by distillation and the residue, consisting mainly of quadricyclane but with a small amount of unreacted norbornadiene, was purified by fractional distillation under reduced pressure. The more volatile norbornadiene was mainly concentrated in the fore-run, which was discarded and, by repeated fractionation, quadricyclane (10 g, 51%) with a purity of greater than 99% was obtained. The 300 MHz  $^1\text{H}$  NMR spectrum showed d 2.02 (2H, t,  $J = 1.5$  Hz,  $\text{CH}_2$ ), 1.48–1.50 (4H, m) and 1.34–1.38 ppm (2H, m) in agreement with the literature,<sup>3,4</sup> with the residual norbornadiene signal at 6.77 ppm corresponding to a proportion of 0.5%.

1. C. D. Smith, *Org. Synth.* 51, 133–135 (1971). <https://doi.org/10.15227/orgsyn.051.0133>

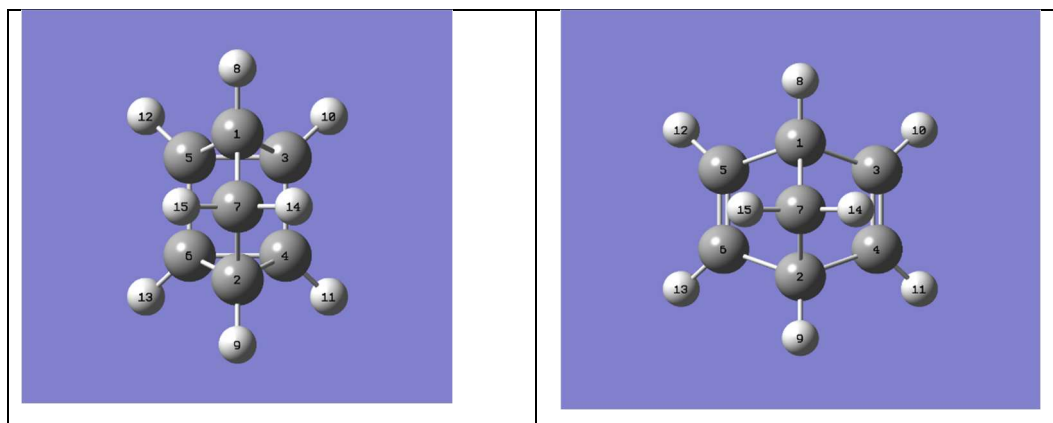
2. G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.* 83, 4674–4675 (1961). <https://doi.org/10.1021/ja01483a051>

3. W. G. Dauben and R. L. Cargill, *Tetrahedron* 15, 197–201 (1961). [https://doi.org/10.1016/0040-4020\(61\)80026-4](https://doi.org/10.1016/0040-4020(61)80026-4)

4. L. Pan, R. Feng, H. Peng, X. E, J.-J. Zou, L. Wang, and X. Zhang, *RSC Adv.* 4, 50998–51001 (2014). <https://doi.org/10.1039/c4ra08868a>

**SM2: The GIAO calculated  $^1\text{H}$  and  $^{13}\text{C}$  magnetic shielding and spin-spin coupling constants.**

**Figure SM2.1 The atom numbering schemes for the NMR spin coupling constants**



**Table SM2.1 H- and C-nuclei magnetic shielding for quadricyclane, calculated by GIAO methods, compared with experimental results. Shifts relative to tetramethylsilane (TMS) under the same conditions. APFD results are corrected by 0.07 ppm, using our new TMS data as reference nucleus.**

QC	Method/Centres	H1,4	H2,3,5,6	H7
	Present NMR	1.360	1.490	2.020
	APFD/6-311G[2d,1p]	1.28	1.42	2.15
	B3LYP/Def2-TZVPPD	1.43	1.62	2.28
	B3LYP/EPR-III	1.33	1.53	2.17
		C1,4	C2,3,5,6	C7
	NMR <sup>35,36</sup>	23.04 <sup>35,36</sup>	14.77 <sup>35,36</sup>	32.03 <sup>35,36</sup>
	Q-COSY 2D NMR <sup>71</sup>	22.6	14.4	31.6
	APFD/6-311G[2d,1p]	21.22	12.11	30.02
	B3LYP/Def2-TZVPPD	25.57	16.07	35.18
	B3LYP/EPR-III	29.08	19.24	38.80
NBD	Method/Centres	H1,4	H2,3,5,6	H7
$\delta$ from TMS/ppm	Present + NMR <sup>75</sup>	3.57	6.76	1.98
	APFD/6-311G[2d,1p]	3.70	7.25	2.32
	B3LYP/EPR-III	3.69	7.28	2.24
		C1/2	C3/4/5/6	C7
	Present NMR	50.215	143.37	75.28
	NMR <sup>75</sup>	50.27	143.42	75.33
	B3LYP/EPR-III	50.78	159.30	87.25

#### Footnotes to Table SM2.1

30. R. T. Boéré, J. A. Eng, K. Preuss, M. Parvez, C. D. Bryan, and A. W. Cordes, *Can. J. Chem.* **72**, 1171–1180. <https://doi.org/10.1139/v94-150>

35. O. Baumgärtel and G. Szeimies, *Chem. Ber.* **116**, 2180–2204 (1983). <https://doi.org/10.1002/cber.19831160612>

36. P. L. Beaulieu, A. Kabo, and D. G. Garratt, *Can. J. Chem.* **58**, 1014–1020 (1980). <https://doi.org/10.1139/v80-159>

71. C. Aroulanda, P. Lesot, D. Merlet, and J. Courtieu, *J. Phys. Chem. A* **107**, 10911–10918 (2003). <https://doi.org/10.1021/jp030137m>

**Table SM2.2 The full spin coupling constant matrix (Hz) as lower triangle.**

QRC.b3lyp.APFD+6-311+G[2d,p].GIAO.NMR					
--	C1	C2	C3	C4	C5
C1	0.00	--	--	--	--
C2	2.03	0.00	--	--	--
C3	11.09	-0.27	0.00	--	--
C4	-0.27	11.09	42.59	0.00	--
C5	11.09	-0.27	8.34	-6.58	0.00
C6	-0.27	11.09	-6.58	8.34	42.59
C7	40.02	40.02	0.54	0.54	0.54
H1	148.46	8.75	0.81	3.22	0.81
H2	8.75	148.46	3.22	0.81	3.22
H3	-0.81	0.26	162.91	2.53	-2.73
H4	0.26	-0.81	2.53	162.91	2.62
H5	-0.81	0.26	-2.73	2.62	162.91
H6	0.26	-0.81	2.62	-2.73	2.53
H7	-3.33	-3.33	0.59	0.59	6.85
H8	-3.33	-3.33	6.85	6.85	0.59
--	C6	C7	H8	H9	H10
C6	0.00	--	--	--	--
C7	0.54	0.00	--	--	--
H1	3.22	4.34	0.00	--	--
H2	0.81	4.34	0.76	0.00	--
H3	2.62	0.73	4.29	-0.72	0.00
H4	-2.73	0.73	-0.72	4.29	1.83
H5	2.53	0.73	4.29	-0.72	5.23
H6	162.91	0.73	-0.72	4.29	1.13
H7	6.85	117.98	1.33	1.33	-0.39
H8	0.59	117.98	1.33	1.33	-0.53
--	H11	H12	H13	H14	H15
H4	0.00	--	--	--	--
H5	1.13	0.00	--	--	--
H6	5.23	1.83	0.00	--	--
H7	-0.39	-0.53	-0.53	0.00	--
H8	-0.53	-0.39	-0.39	-10.49	0.00

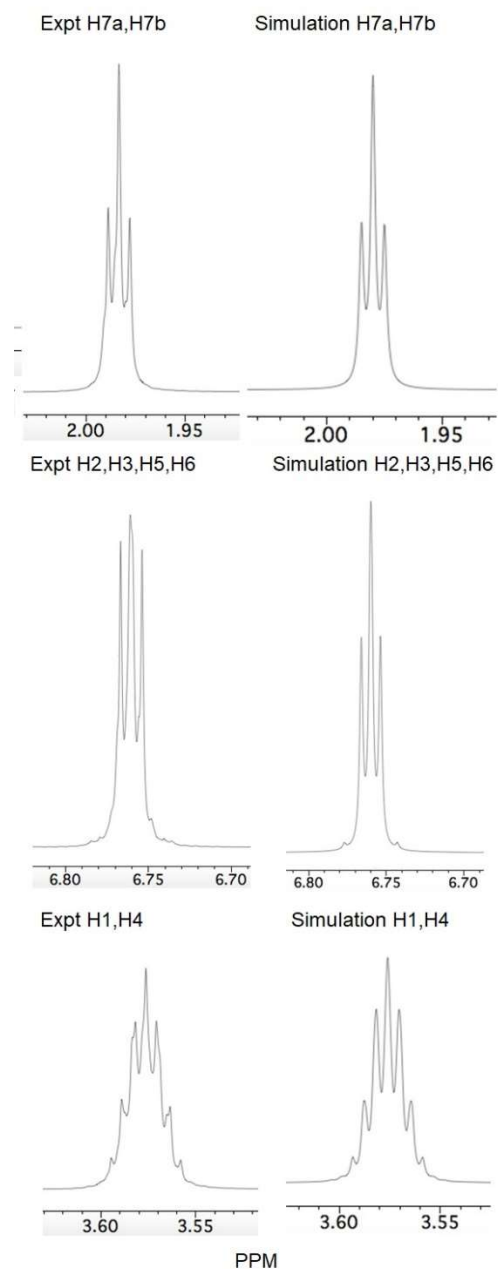
**Table SM2.3  $^1\text{H}^1\text{H}$ ,  $^{13}\text{C}^1\text{H}$  and  $^{13}\text{C}^{13}\text{C}$  spin coupling constants for QC by determined by GIAO methods. These are the only unique values, and the chemically equivalent but magnetically non-equivalent values are numerically the same.**

Methods used: (A) APFD; 6-311G[2d,p]; (B) B3LYP;Def2-TZVPPD; (C) B3LYP;EPR-III

$^{13}\text{C}^1\text{H}$ couplings					$^1\text{H}^1\text{H}$ couplings				
Centre	A	B	C	Expt	Centre	A	B	C	Expt

CH1	148.46	159.56	170.00	165.9, <sup>36</sup> 166.0, <sup>37</sup>	H1,4	0.76	0.93	1.20	
C1H4	8.75	9.30	9.63		H1,2	4.29	4.23	5.47	4.3
C1H2	-0.81	-0.28	-0.26		H1,3	-0.72	-0.75	-0.62	
C1H3	0.26	0.35	0.40		H1,7	1.33	1.32	1.63	1.5
C1H7	-3.33	-2.21	-2.56		H2,3	1.83	1.73	2.80	2.5
C2H1	0.81	1.85	1.83		H2,6	5.23	4.91	6.50	5.0
C2H4	3.22	3.46	3.65		H2,5	1.13	1.04	1.50	
C2H2	162.91	177.54	189.22	183.2, <sup>36</sup> 184.7, <sup>37</sup>	H2,7a	-0.39	-0.43	-0.34	
C2H3	2.53	3.88	3.94		H2,7b	-0.53	-0.51	-0.34	
C2H6	-2.73	-2.58	-2.50		H7a,7 b	-10.49	-8.92	-11.10	
C2H5	2.62	2.61	2.71						
C2H7a	0.59	0.59	0.67						
C2H7b	6.85	7.29	7.71						
C7H7	117.98	125.39	133.95	132.2, <sup>36</sup> 131.4, <sup>37</sup>					

**Figure SM2.2 The 300 MHz <sup>1</sup>H NMR spectrum of norbornadiene. Weak 2<sup>nd</sup> order effects are still visible at this frequency for H1 and H4.**



**SM3. Fits to the lowest two ionization energies for norbornadiene and quadricyclane and the combined 3rd state of QC.**

**Table SM3.1 (a) norbornadiene.**

Peak	Location	Area	FWHM
0	8.380(2)7	26(8)	0.025(6)
1	8.428(1)	60(10)	0.026(3)
2	8.4765(4)	132(20)	0.025(1)
3	8.5260(2)	230(20)	0.023(1)
4	8.5742(1)	373(20)	0.024(1)
5	8.6218(1)	484(20)	0.024(1)
6	8.6694(1)	604(30)	0.025(1)
7	8.7166(1)	600(40)	0.027(1)

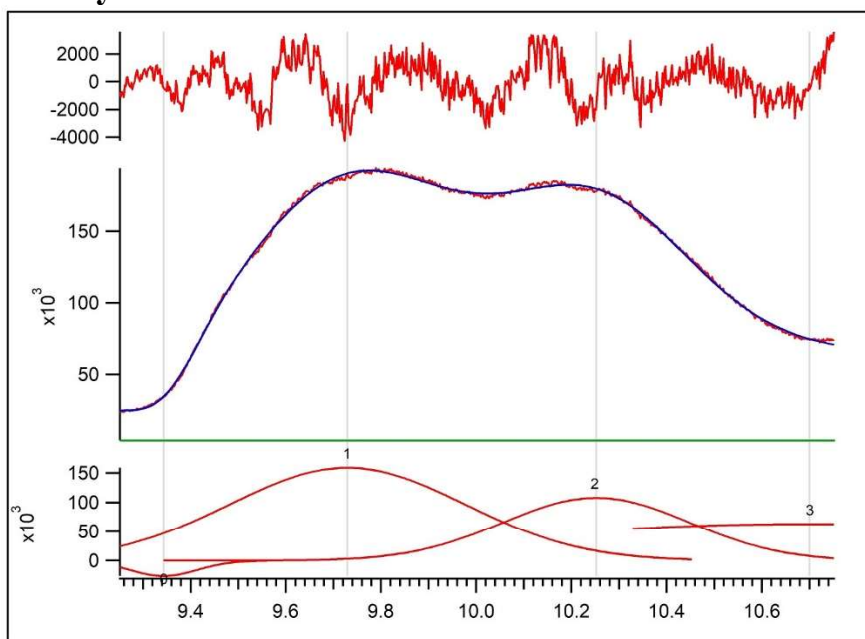
8	8.7633(1)	518(30)	0.025(1)
9	8.8098(2)	404(30)	0.025(1)
10	8.8569(2)	326(30)	0.025(1)
11	8.9039(3)	232(30)	0.025(1)
12	8.9500(4)	202(30)	0.027(2)
13	8.9969(4)	154(30)	0.027(3)
14	9.0429(6)	129(30)	0.028(4)
15	9.090(1)	68(20)	0.027(5)
16	9.134(1)	42(20)	0.026(6)
17	9.189(2)	32(10)	0.030(9)
18	9.265(3)	9(6)	0.012(8)
A	8.60(3)	513(500)	0.175(6)
B	8.80(3)	3850(650)	0.37(4)
C	9.20(3)	717(100)	0.30(5)
a	9.403(1)	164 (10)	0.05(5)
b	9.484(2)	1135(70)	0.16(5)
c	9.704(8)	3350(200)	0.46(5)
d	9.587(4)	3185(100)	0.27(5)

**Table SM3.2 (b) Quadricyclane. Fit to the lowest ionization energy for quadricyclane contaminated by norbornadiene (NBD); the lines for NBD are bands 12 to 27 and are shown in yellow.**

Band	Location	LocSigma	Area	AreaSigma	FWHM	FWHMSigma
0	7.67064	0.003	0.000308209	0.0001	0.035	0.008
1	7.75781	0.001	0.00129607	0.0003	0.044	0.005
2	7.84479	0.001	0.00313179	0.0008	0.052	0.005
3	7.93123	0.001	0.00536321	0.002	0.060	0.007
4	8.01593	0.001	0.00639327	0.004	0.06	0.01
5	8.09901	0.002	0.00550299	0.006	0.07	0.02
6	8.18081	0.007	0.00290482	0.004	0.07	0.02
7	8.22047	0.008	0.00035449	0.0008	0.03	0.02
9	8.27531	0.005	0.000825529	0.0007	0.04	0.01
10	8.36288	0.009	0.000708981	0.0007	0.067	0.03
12	8.47176	0.002	0.000262454	0.0001	0.0233	0.006
13	8.5254	0.001	0.000527695	0.0001	0.0233	0.004
14	8.57375	0.0006	0.000946037	0.0002	0.0233	0.003
15	8.62049	0.0004	0.00159538	0.00034	0.0259	0.002
16	8.66732	0.000	0.0018996	0.0004	0.0274	0.002
17	8.71411	0.0004	0.00183866	0.0004	0.0287	0.003
19	8.76124	0.0004	0.00141885	0.0003	0.0238	0.002
20	8.80752	0.0006	0.00100564	0.0002	0.0233	0.002
21	8.85685	0.0009	0.000797044	0.0002	0.0235	0.003
22	8.90354	0.0009	0.000888061	0.0004	0.0256	0.005
23	8.95041	0.002	0.00126596	0.001	0.0333	0.009
24	8.9926	0.003	0.00105945	0.001	0.0333	0.009
25	9.03486	0.005	0.00136205	0.002	0.0453	0.03
26	9.08265	0.009	0.000898695	0.002	0.044	0.02
27	9.12924	0.005	0.000326937	0.0005	0.031	0.02

A	8.297	0.2	0.22887	0.2	0.4	0.1
B	8.56059	0.2	0.122367	0.50	0.3	0.4
C	8.81321	0.3	0.0847578	0.4	0.3	0.6
D	9.19151	0.2	0.0419084	0.2	0.4	1.5

**Figure SM3.1 (c) Fit to the double maximum between 9.75 and 10.2 eV for Quadricyclane.**



Location	LocSigma	Amplitude	AmpSigma	Area	AreaSigma	FWHM	FWHMSigma
9.34331	0.0034923	-26234.8	3026.94	-4650	800.747	0.166511	0.0100202
9.72936	0.0108647	159000	75179.1	98486.6	59058.3	0.581898	0.0739917
10.2526	0.00200897	107535	30772.4	52942.6	17267.9	0.462511	0.019093
10.7	0.308998	62851.9	64477.7	111402	350658	1.66511	3.53754

Y data wave: root:Counts

X data wave: root:BE

Chi square: 1.5733e+09

Total fitted points: 751

Multi-peak fit version 2.22

Total Peak Area = 2.5818e+05 +/- 3.5602e+05

**SM4. Comparison of the molecular structures of NBD and QC with experimental microwave and other spectral data.** Several electron diffraction (ED),<sup>61-63</sup> nematic phase nuclear magnetic resonance (NP-NMR)<sup>64-66</sup> and microwave spectroscopy (MW) papers,<sup>67-69</sup> have focused on NBD with few on QC.<sup>70,71</sup> A comparison of the bond lengths, rotational constants (RC) and quartic centrifugal distortion constants (QCDC) for neutral NBD in its MW substitution structure<sup>68</sup> are compared with the present equilibrium structural theoretical values, determined at both the CCSD(T) and MP4(SDQ) levels in the Rotational constants (A, B, C), give a relative measure of the overall shape, via the moments of inertia. The CCSD(T) data shows very close RC values for both NBD<sup>68</sup> and QC,<sup>71</sup> which differ from the MW data by less

than 1%. The results from the MP4(SDQ) ground state calculations, differ from the experimental data by a further small amount.

We are unable to compute the QCDC beyond the MP2 level with G-16. However, even at the Hartree-Fock level, the values are close to those from the microwave spectra. For NBD, our values, compared with the MW ones in parentheses,<sup>67</sup> are:  $\Delta_J$ : 0.323 (0.311(17)),  $\Delta_{JK}$ : -0.0618 (-0.076(6)),  $\Delta_K$ : 0.249 (0.2684(7)),  $\delta_J$ : 0.00681 (0.00478(7)) and  $\delta_K$ : 0.0822 (0.0922(6)) kHz. The corresponding data for QC<sup>71</sup> with the MW results in parentheses are:  $\Delta_J$ : 0.406 (0.267(13)),  $\Delta_{JK}$ : -0.140 (0.2157(10)),  $\Delta_K$ : -0.075 (-0.0732(7)),  $\delta_J$ : 0.0111 (0.00477(2)) and  $\delta_K$ : 0.892 (0.0100(4)) kHz. The dipole moments (Debye (D)) for NBD and QC differ experimentally by a factor of 3, with values NBD ( $\mu_C$ ) 0.05866(9) and QC ( $\mu_B$ ) 0.01989(18) D; our values are NBD: 0.0291 D and QC: 0.0086 D.

In summary, we believe that the calculated ground state properties above, are sufficiently close to experiment, to give confidence that the ionization energy calculations for the ionic states, where there is no experimental data, can be relied upon. The ionic state RC values determined at the MP4(SDQ) level in Tables I and II, show some variation with electronic state. For all the  $C_{2v}$  states of NBD except  ${}^2A_2$ , the double bonds are still apparent; but for the other symmetry states, there is lengthening of bonds, with weakening the bridge  $CH_2$  bridge ( ${}^2A_1$  and  ${}^2B_2$ ), and for breaking the C=C bonds ( ${}^2A_2$  state). Further details of the structures are given in the supplementary material as SM5.

64. J. W. Emsley J. C. Lindon, *Mol. Phys.* **29**, 531–538 (1975). <https://doi.org/10.1080/00268977500100441>

65. K. C. Cole and D. F. R. Gilson, *J. Mol. Struct.* **82**, 71–75 (1982). [https://doi.org/10.1016/0022-2860\(82\)85235-6](https://doi.org/10.1016/0022-2860(82)85235-6)

66. W. A. Heeschen, D. W. Alderman, and D. M. Grant, *J. Phys. Chem.* **92**, 6504–6511 (1988). <https://doi.org/10.1021/j100334a008> .

67. G. Knuchel, G. Grassi, B. Vogelsanger, and A. Bauder, *J. Am. Chem. Soc.* **115**, 10845–10848 (1993). <https://doi.org/10.1021/ja00076a047>

68. B. Vogelsanger and A. Bauder, *J. Mol. Spectrosc.* **130**, 249–257 (1988). [https://doi.org/10.1016/0022-2852\(88\)90298-6](https://doi.org/10.1016/0022-2852(88)90298-6)

69. J. Demaison J. Vogt G. Wlodarczyk ‘Rotational and Related Constants of Diamagnetic Asymmetric Top Molecules’; 1. Introduction: Landolt-Börnstein - Group II Molecules and Radicals; Vol. **19B** (Rotational and Related Constants of Diamagnetic Asymmetric Top Molecules). W. Hüttner (ed.) SpringerMaterials (1992);

[http://materials.springer.com/lbdocssm\\_lbs\\_978-3-540-69986-6\\_1](http://materials.springer.com/lbdocssm_lbs_978-3-540-69986-6_1); (Springer-Verlag Berlin Heidelberg 1992). [https://doi.org/10.1007/10048563\\_1](https://doi.org/10.1007/10048563_1)

70. B. Vogelsanger and A. Bauder, *J. Mol. Spectrosc.* **136**, 62–67 (1989). [https://doi.org/10.1016/0022-2852\(89\)90219-1](https://doi.org/10.1016/0022-2852(89)90219-1)

71. C. Aroulanda, P. Lesot, D. Merlet, and J. Courtieu, *J. Phys. Chem. A* **107**, 10911–10918 (2003). <https://doi.org/10.1021/jp030137m>

72. D. W. Rogers and F. J. McLafferty, *J. Phys. Chem. A* **103**, 8733–8737 (1999). <https://doi.org/10.1021/jp992093g>

73. K. Raghavachari, R. C. Haddon, and H. D. Roth, *J. Am. Chem. Soc.* **105**, 3110–3114 (1983). <https://doi.org/10.1021/ja00348a026>

74. I. W. Levin and W. C. Harris, *Spectrochim. Acta* **29A**, 1815–1834 (1973). [https://doi.org/10.1016/0584-8539\(73\)80167-9](https://doi.org/10.1016/0584-8539(73)80167-9)



### SM5. The ground state equilibrium structures of NBD and QC.

(a) TZVP B3LYP NBD CCCSD(T) equilibrium structure

C 0. 1.123090202 0.2591606837  
 C 0. -1.123090202 0.2591606837  
 C 1.2390527604 0.6712353449 -0.5360381039  
 C 1.2390527604 -0.6712353449 -0.5360381039  
 C -1.2390527604 0.6712353449 -0.5360381039  
 C -1.2390527604 -0.6712353449 -0.5360381039  
 C 0. 0. 1.3368772591  
 H 0. 2.1577465619 0.6038314618  
 H 0. -2.1577465619 0.6038314618  
 H 1.9216516652 1.3371482915 -1.0505201754  
 H 1.9216516652 -1.3371482915 -1.0505201754  
 H -1.9216516652 1.3371482915 -1.0505201754  
 H -1.9216516652 -1.3371482915 -1.0505201754  
 H 0.9032144492 0. 1.9547557837  
 H -0.9032144492 0. 1.9547557837

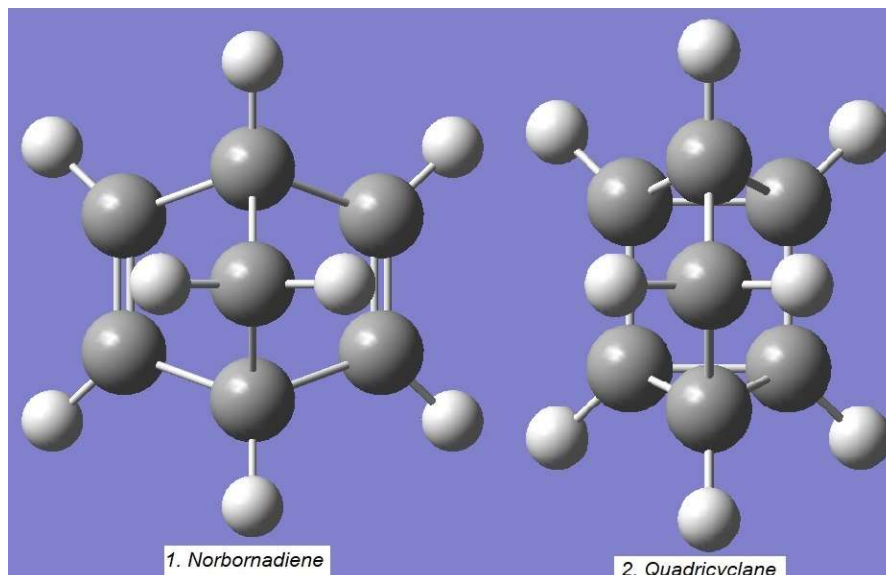
(b) Quadricyclane TZVP CCSD(T) equilibrium structure

C 0.7607988114 0.7741426693 -0.7086067421  
 C 0.7607988114 -0.7741426693 -0.7086067421  
 C -0.7607988114 0.7741426693 -0.7086067421  
 C -0.7607988114 -0.7741426693 -0.7086067421  
 C 0.0000000000 1.1500873738 0.5508804329  
 C 0.0000000000 -1.1500873738 0.5508804329  
 C 0.0000000000 0.0000000000 1.5368636948  
 H 1.4501675598 1.4277904879 -1.2267130055  
 H 1.4501675598 -1.4277904879 -1.2267130055  
 H -1.4501675598 1.4277904879 -1.2267130055  
 H -1.4501675598 -1.4277904879 -1.2267130055  
 H 0.0000000000 2.1864147953 0.8713701518  
 H 0.0000000000 -2.1864147953 0.8713701518  
 H -0.8930505437 0.0000000000 2.1727390632  
 H 0.8930505437 0.0000000000 2.1727390632

**Table SM5.1 Comparison of the bond lengths between the ground and ionic states.**

Norborene							
	X <sup>1</sup> A <sub>1</sub>	X <sup>1</sup> A <sub>1</sub>	X <sup>1</sup> A <sub>1</sub>	<sup>2</sup> A <sub>1</sub>	<sup>2</sup> B <sub>1</sub>	<sup>2</sup> B <sub>2</sub>	<sup>2</sup> A <sub>2</sub>
Method	Nematic phase NMR + ED <sup>39</sup>	MP4(SDQ)	MP2	MP2	MP2	MP2	MP2
C=C	1.339	1.3368	1.3468	1.3708	1.3867	1.3414	1.3159
C-C	1.533	1.5387	1.5361	1.5070	1.5192	1.5266	1.5964
C-C <sub>7</sub>	1.571	1.5520	1.5543	1.6191	1.5456	1.6359	1.5493
-C-H	1.108	1.0879	1.0912	1.0848	1.0870	1.0824	1.0905
=C-H	1.090	1.0803	1.0839	1.0891	1.0857	1.1124	1.0927
C <sub>7</sub> -H	1.110	1.0915	1.0946	1.0890	1.0867	1.0899	1.0894

Figure SM5.1. The equilibrium structures of the  $X^1A_1$  ground states of NBD and QC in same scale diagrams, which show the much more compact QC system, owing to the  $C_1C_2C_6$  and  $C_3C_4C_5$  being close to  $60^\circ$  in the double cyclopropane system. The CCSD(T) energies are  $-270.96099960$  a.u. (NBD) and  $-270.92372136$ a.u. (QC), making NBD more stable than QC by  $0.0373$  a.u. ( $1.0144$  eV).



### SM6. Vibration frequencies of the ground and ionic states.

Table SM6.1 MP2 mode sequences for norbornadiene in ascending frequency as used in the Franck-Condon profiles of active modes in Table VI.

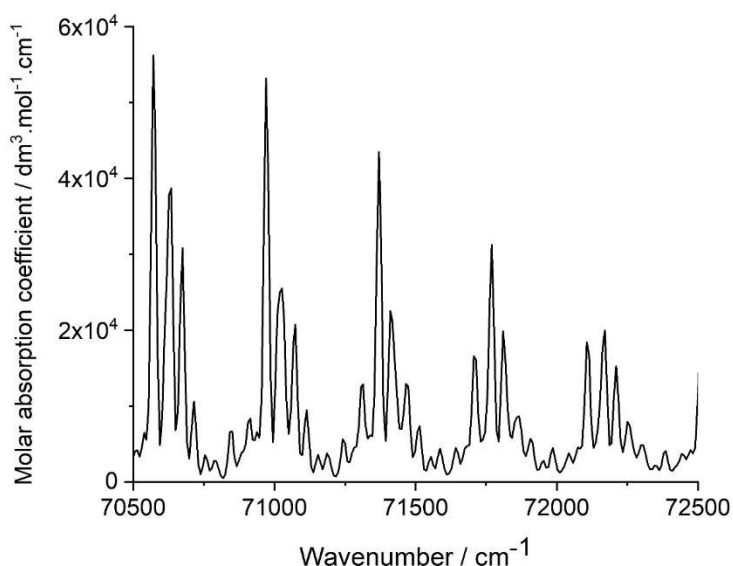
$X^1A_1$			$^2B_1$		
1	2	3	1	2	3
A1	A2	B1	A2	A1	B1
428.7820	451.2112	510.7976	391.9949	398.9584	457.8472
4	5	6	4	5	6
B2	B1	A2	B2	A2	B1
553.6956	680.7807	719.5441	696.8263	718.1374	745.8546
7	8	9	7	8	9
A1	A1	B2	A1	A1	B2
729.6216	794.3051	820.7068	781.9165	839.4109	887.8238
10	11	12	10	11	12
B2	A1	A2	B1	A1	B2
896.1775	904.1713	908.9075	889.9211	923.0149	928.5706
13	14	15	13	14	15
B2	B1	A2	A2	A2	A1
919.0565	931.9095	945.1581	959.1858	973.4081	1012.6945
16	17	18	16	17	18
A1	B2	B1	B2	B1	B1
967.0586	975.9987	1046.3067	1018.9770	1023.3940	1097.9017
19	20	21	19	20	21
B1	A1	A2	A1	A2	B1
1091.4754	1138.3153	1145.4619	1131.8955	1171.8815	1208.9349

22	23	24	22	23	24
B2	B1	A1	B2	A2	B2
1151.5328	1246.6535	1258.3734	1224.8502	1261.5655	1274.6263
25	26	27	25	26	27
B2	A2	A2	A1	A2	B2
1285.6919	1286.3204	1311.7450	1292.2536	1305.1207	1372.1832
28	29	30	28	29	30
B2	A1	B1	A1	B2	A1
1356.4681	1513.1598	1576.7804	1502.6562	1536.9121	1537.0939
31	32	33	31	32	33
A1	A1	B1	B1	A1	B1
1614.9016	3095.8888	3169.3471	2010.7538	3106.7594	3187.6501
34	35	36	34	35	36
B2	A1	A2	B2	A1	A2
3171.3405	3173.5252	3249.1317	3220.7631	3220.8477	3251.7495
37	38	39	37	38	39
B2	B1	A1	B2	A1	B1
3250.5399	3274.6747	3276.7044	3252.7394	3264.4626	3264.7562
${}^2B_2$					
1	2	3			
B1	A2	A1			
368.1507	417.1058	428.6114			
4	5	6			
B2	B2	B1			
484.5299	644.2488	657.1770			
7	8	9			
A1	A1	A2			
671.7481	711.4750	717.1386			
10	11	12			
A1	B2	A2			
795.8606	818.9600	871.9375			
13	14	15			
A2	B2	A2			
915.8341	916.8094	941.5183			
16	17	18			
B1	B2	A1			
944.8559	947.3660	969.2265			
19	20	21			
B1	B1	A1			
970.0712	1083.1607	1109.8522			
22	23	24			
B2	B1	A2			
1149.4485	1162.2545	1180.0682			
25	26	27			
A1	A2	B2			
1196.2246	1286.1853	1311.0492			
28	29	30			
A1	B1	A1			

1483.0739	1576.8679	1618.8539
31	32	33
B2	B2	A1
1819.0857	2916.8391	2951.4037
34	35	36
A1	B1	B2
3149.2039	3264.7891	3266.5050
37	38	39
A2	B1	A1
3266.6328	3286.3748	3288.5249

## SM6.2. Vibrationally excited ionic states

**Figure SM6.1.** The calculated tail of the lowest ionic state of norbornadiene ( $X^2B_1$ ) as shown in Figure 9, where a progressively more complex set of vibrational states is calculated as the energy increases.



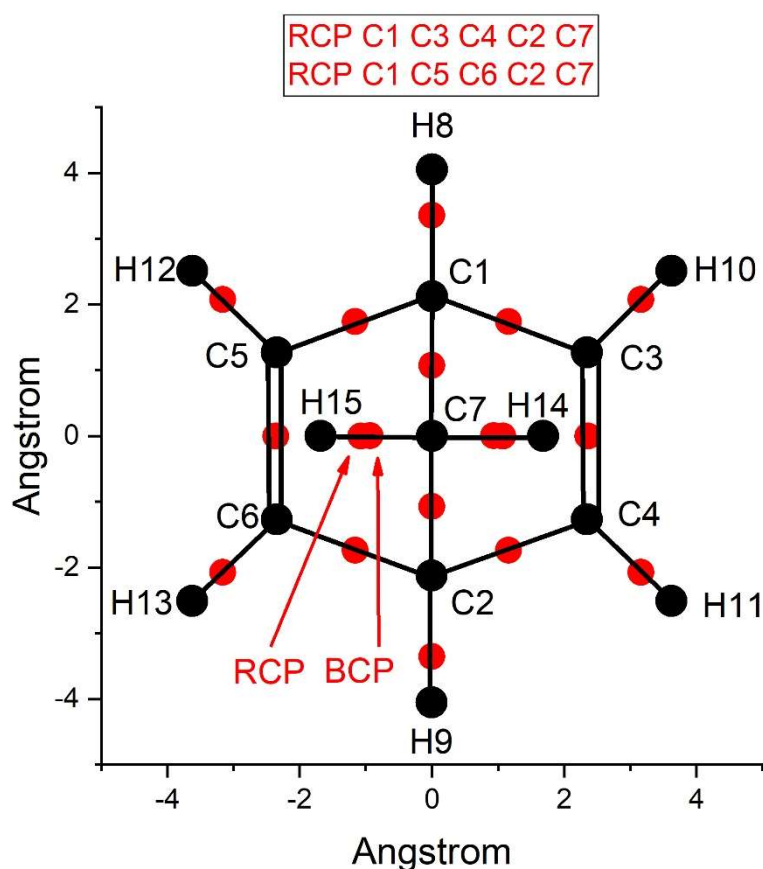
## SM7. Bond and ring critical points.

In this Section we determine local minima of the electron density between bonded atoms, and also within groups of atoms such as local rings. This gives a view to where non-bonded interactions occur. The method used is the quantum theory of atoms in molecules (QTAIM)<sup>87</sup> by Bader et al<sup>88-90</sup> originally designated as AIM. We determine “critical points (CPs)” where the gradient of the electron density along each internuclear distance, including bonds and non-bonding situations, is zero. The CPs are shown in red with the 3-dimensional molecular framework in black.

**(a) Norbornadiene.** All 16 bonds show one bond critical point (BCP) close to the bond midpoint irrespective of single or double bonding; as shown in Figure 12. In addition, two ring critical points (RCP) are found corresponding to the pair of 5-membered rings which include

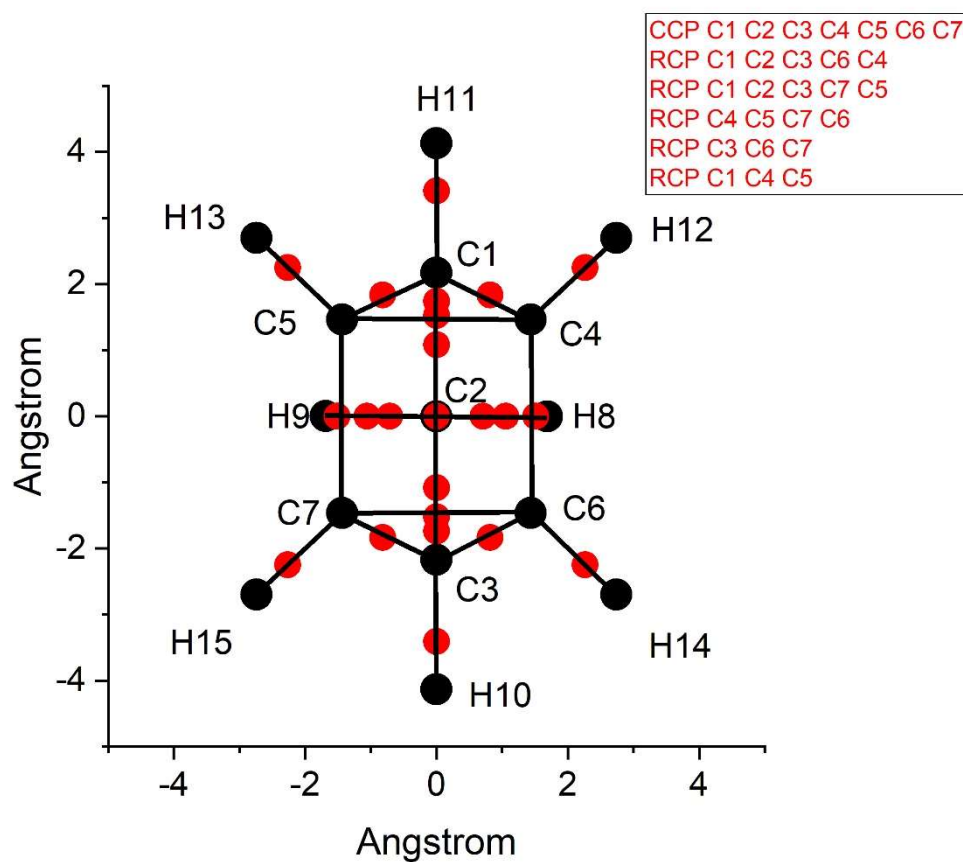
one C-C=C-C unit and the bridging C<sub>7</sub> atom. No RCP is found to lie between the two double bonds in NBD in contrast to QC below.

**Figure SM7.1.** The critical points in the QTAIM analysis of the MP4(SDQ) wave-function for norbornadiene. In the projection shown the two ring critical points appear overlapping but they are well separated in the axis normal to the paper. Since the molecular dipole moment is so small the degree of polarization of the bonds is very small. This leads to the C-C and C=C having the BCP at the mid-point of the bond. However, the C-H bonds do show the CP is much closer to the H-atom than the C-atom in all projections. This shows that the H-atom is locally polarized positive relative to the attached C-atom. This is a direct result of integration of the wave-function and hence is not measured by atomic populations of the constituent atoms.



**(b) Quadricyclane.** This situation is more complex as shown in Figure 13. We have modified the QC ring numbering to follow that generated by QTAIM as in the caption. Since the projections in Figures 12 and 13 are the same, the BCP for NBD and QC appear to lie in very similar positions; but these differ in the 3-dimensional cage structures. Five RCP are found for QC; one for each 3, 4 and 5-membered ring with the atoms involved shown in the Figure 13 caption. A 4-membered RCP lies directly below C<sub>7</sub> in the current projection and hence is not visible here.

**Figure SM7.2.** The quadricyclane critical points superimposed on the molecular skeleton. Each bonded pair of atoms produce a CP. The cyclopropane units each produce a RCP as does the cyclobutene unit here atoms C<sub>4</sub>C<sub>5</sub>C<sub>6</sub>C<sub>7</sub>. As with NBD two RCP occur with the 5-membered ring structure which includes the bridgehead CH<sub>2</sub> unit. The closely spaced pairs of CP across including the CH<sub>2</sub> unit are the local C-H CP and the 5-membered RCP. The single cage CCP is shown superimposing C<sub>2</sub> but lies below it in another projection.



87. AIMAll (Version 19.10.12) T. A. Keith TK Gristmill Software Overland Park KS USA 2019. <http://aim.tkgristmill.com>

88. R. F. W. Bader, *Acc. Chem. Res.* **8**, 34–40 (1975). <https://doi.org/10.1021/ar50085a005>

89. R. F. W. Bader, *Chem. Rev.* **91**, 893–928 (1991). <https://doi.org/10.1021/cr00005a013>

90. R. F. W. Bader *Atoms in Molecules-A Quantum Theory* (Oxford University Press, Oxford, 1990).