Electronic Supplementary Information to

The ortho-Benzyne Cation is Not Planar

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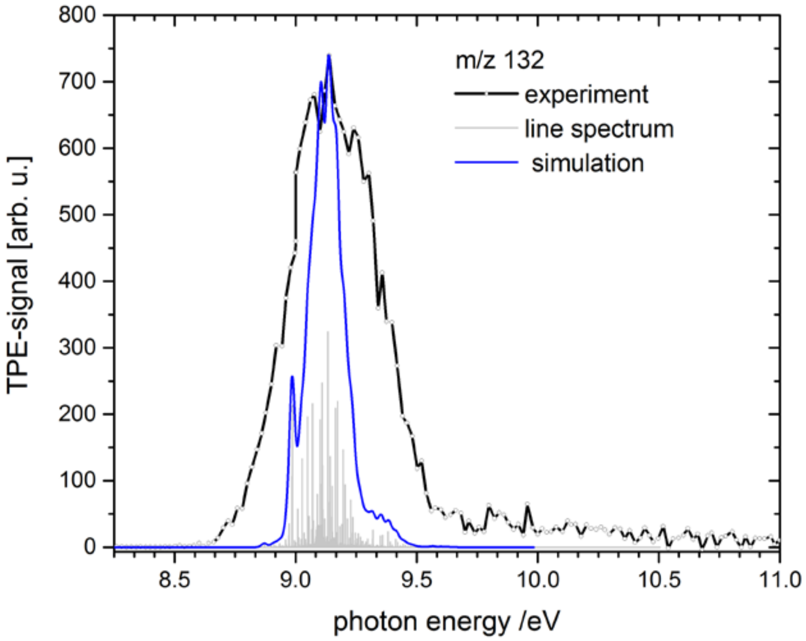


Figure S1: Mass-selected threshold photoelectron spectrum of benzocyclobuten-1,2-dion. The photon energy was scanned in 10 meV steps, one point was averaged for 120 s. From the Franck-Condon simulation (blue envelope) we assume an IE_{ad} of 8.96 eV. An experimental IE_{vert}=9.23 was reported by Gleiter *et al*,[1] computations yielded IE_{ad}=9.03 eV. These literature values are thus in good agreement with our experiments.

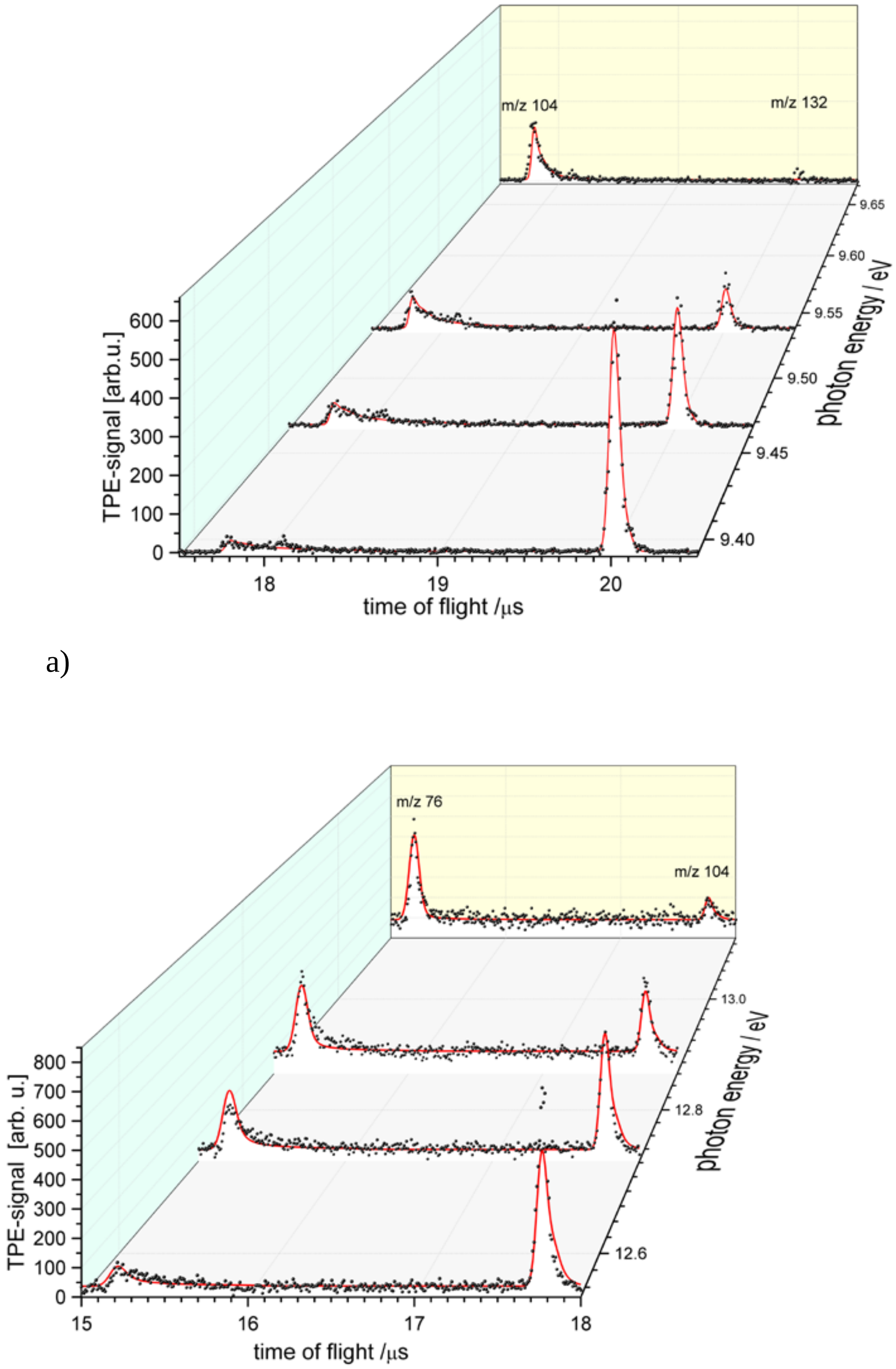


Figure S2: The asymmetry in the daughter TOF distributions for a) the first and b) the second dissociation step indicates a slow rate for the sequential dissociative photoionisation of benzocyclobuten-1,2-dion. The red lines show the simultaneous fit of the experimental TOF distributions (black dots). In the upper trace a small signal from a previous experiment is visible at 18.1 µs.

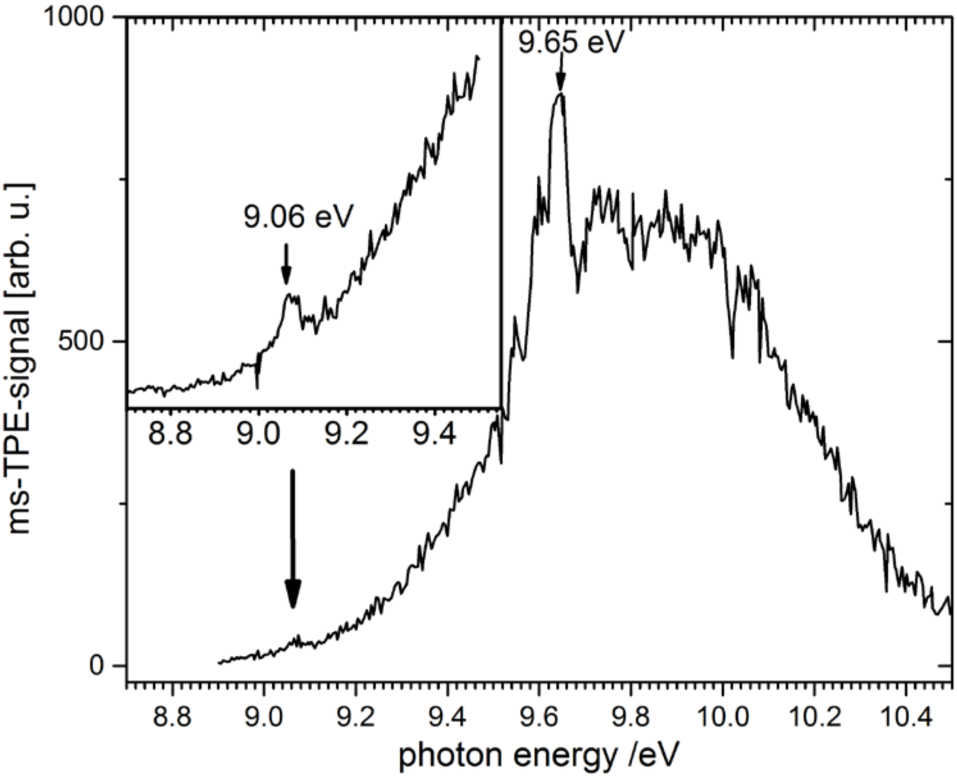


Figure S3: Mass-selected threshold photoelectron (ms-TPE) spectrum of ortho-benzyne with a close-up that shows a small peak at 9.03 eV.

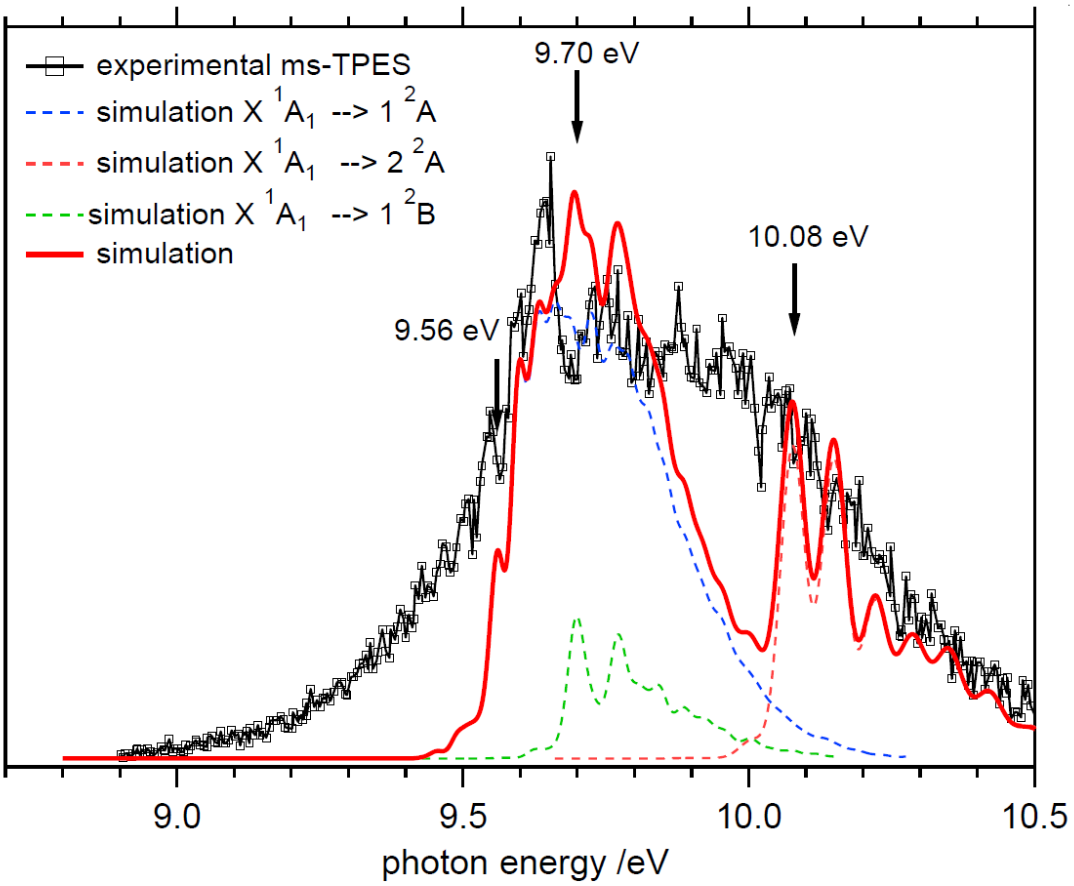


Figure S4: ms-TPE spectrum together with a simulation based on the computed ionization energies. It shows that the computed values are slightly too high. When compared with best simulation, given in Figure 7 in the manuscript, error bars of +50/-100 meV are assumed for IE_{ad} and ±20 meV for the transition into the 1 ^2B state.

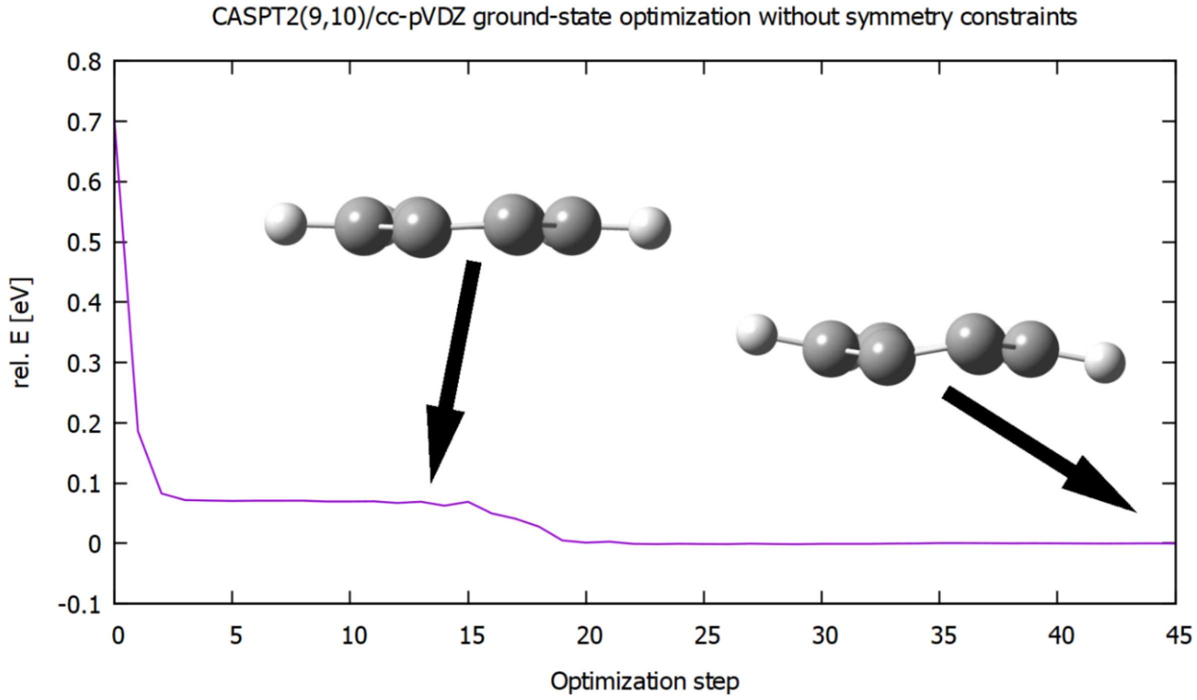


Figure S5: Optimisation of the ortho-benzyne cation without symmetry constraints.

Results of a numerical CASPT2(9,10)/cc-pVDZ geometry optimisation without symmetry constraints for the ground-state of the ortho-benzyne cation, starting from the equilibrium geometry of ortho-benzyne at the SCS-CC2/def2-TZVPP level of theory. It is shown how the optimization procedure seems to converge on a planar structure, most likely the equilibrium geometry of the 1 ^{2}B state, but then reaches an energetically more favorable geometry with a twisted structure.

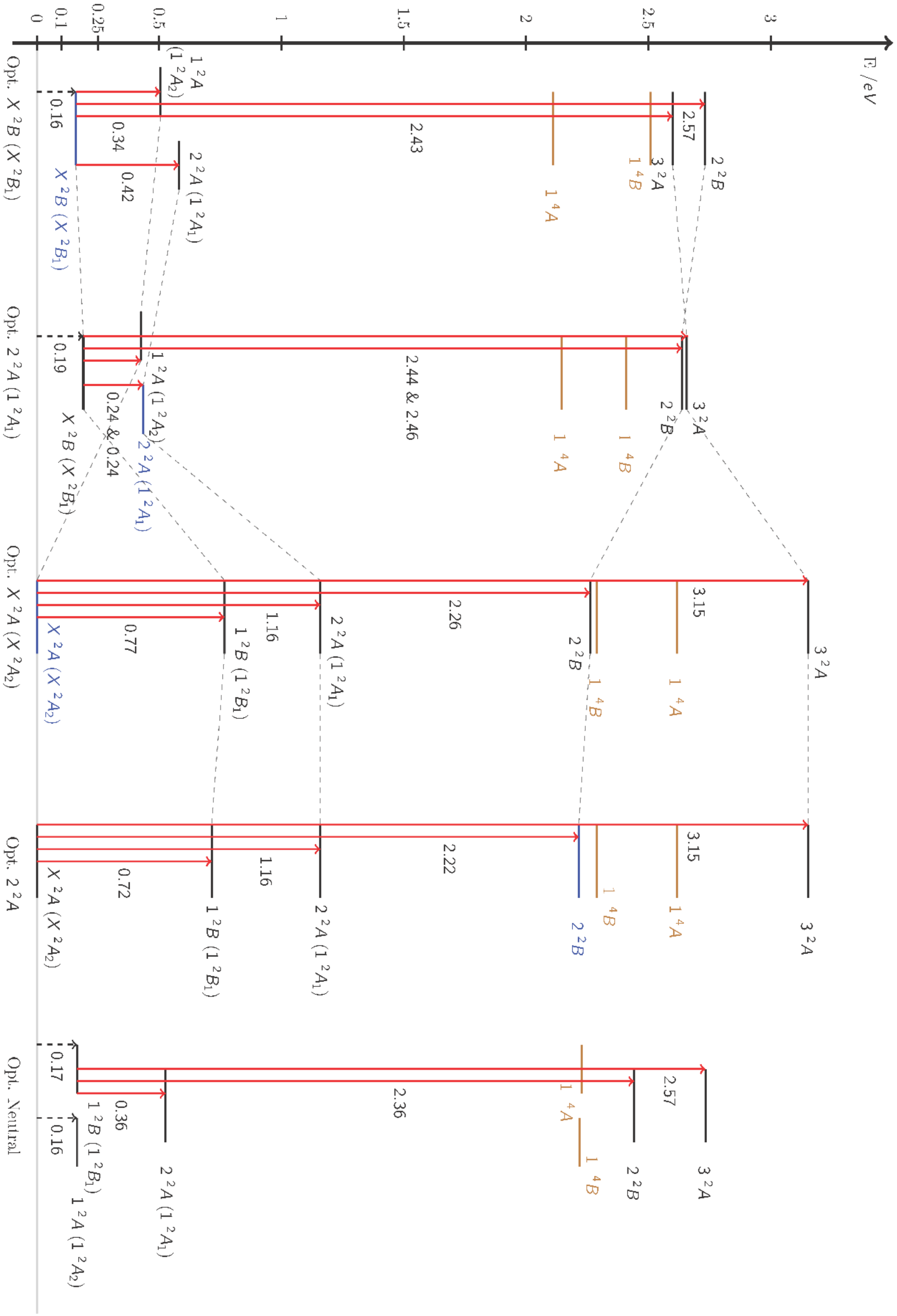


Figure S6: Diagram of all calculated vertical excitation energies at all geometries.

Single-point energy calculations were performed at the SA-MS-CASPT2(11,14)/cc-pVQZ level of theory, solving for the first three roots of each symmetry in C_2 symmetry. Geometries where obtained from optimisations employing (SA-MS-)CASPT2(9,10)/cc-pVDZ (see main article). The state for which the geometry is a minimum equilibrium geometry is indicated in blue.

Table S1: Key parameters for the equilibrium geometries of the ground states of ortho-benzyne and the ortho-benzyne cation, as well as the first three excited states of the ortho-benzyne cation. The numbering of the carbon atoms refers to Figure 2 of the main article.

	C_1 - C_2 distance	C_2 - C_3 distance	C_3 - C_4 distance	C_4 - C_5 distance	C_1 - C_2 - C_3 angle	C_1 - C_2 - C_3 - C_4 dihedral
$1\ ^1A_1$	1.280 Å	1.399 Å	1.419 Å	1.418 Å	126.37 °	0.0 °
$1\ ^2B$ ($1\ ^2B_1$)	1.305 Å	1.394 Å	1.416 Å	1.481 Å	128.26 °	0.03 °
$1\ ^2A$ ($1\ ^2A_2$)	1.279 Å	1.407 Å	1.457 Å	1.393 Å	124.13 °	18.32 °
$2\ ^2A$ ($1\ ^2A_1$)	1.319 Å	1.373 Å	1.438 Å	1.402 Å	128.54 °	0.00 °
$2\ ^2B$	1.280 Å	1.409 Å	1.446 Å	1.396 Å	123.93 °	19.11 °

Table S2: Results of unrestricted optimisations using MP2, SCS-MP2, CC2, SCS-CC2, M06-2X, B3LYP and wB97XD with the cc-pVQZ basis starting from different geometries obtained at the CASPT2(9,10)/cc-pVDZ level of theory for the cation and CASPT2(10,10)/cc-pVDZ for the neutral o-benzyne. All DFT methods predict the skewed geometry to be lower in energy compared to planar geometries. MP2 as well as SCS-MP2 fail to predict the twisted geometry as the ground state. Only SCS-CC2 correctly optimizes to the twisted ground-state geometry from all three starting geometries. Frequency calculations have been run for each optimized structure. ΔE refers to energy difference of optimized geometries if two different geometries are yielded.

<table>
<tr><th></th><th>Optimisation starting from equilibrium geometry of $X^+\ ^2A$ ($1\ ^2A_2$) state (twisted)</th><th>Opt. starting from equilibrium geometry of $1\ ^2B$ ($1\ ^2B_1$) state (planar)</th><th>Opt. starting from neutral equilibrium geometry (planar)</th></tr>
<tr><td>MP2</td><td>- Twisted geometry
- 0 imaginary frequencies
- S^2=0.91
- SOMO = a_2</td><td colspan="2">- Planar geometry, ΔE = -0.09 eV
- 0 imaginary frequencies
- S^2=0.75
- SOMO = a_1</td></tr>
<tr><td>wB97xD</td><td>- Twisted geometry
- 0 imaginary frequencies
- S^2=0.77
- SOMO = a_2</td><td colspan="2">- Planar geometry, ΔE = 0.14 eV
- 2 imaginary frequencies (b_2, a_2)
- S^2=0.76 (b_2, a_2)
- SOMO = a_1</td></tr>
<tr><td>B3LYP</td><td>- Twisted geometry
- 0 imaginary frequencies
- S^2=0.76
- SOMO = a_2</td><td colspan="2">- Planar geometry, ΔE = 0.12 eV
- 2 imaginary frequencies (b_2, a_2)
- S^2=0.77
- SOMO = a_1</td></tr>
<tr><td>M06-2X</td><td>- Twisted geometry
- 0 imaginary frequencies
- S^2=0.76
- SOMO = a_2</td><td colspan="2">- Planar geometry, ΔE = 0.064 eV
- 1 imaginary frequency (b_2)
- S^2=0.76
- SOMO = a_1</td></tr>
<tr><td>CC2</td><td colspan="2">- Twisted geometry
- 2 imaginary frequencies (*a1*, *b2*)
- S^2 = 0.96
- SOMO = a_2</td><td>- Planar geometry, ΔE = 0.12 eV
- 4 imaginary frequencies (3 b_2, a_2)
- S^2 = 0.78
- SOMO = a_1</td></tr>
<tr><td>SCS-CC2</td><td colspan="3">- Twisted geometry
- 3 imaginary frequencies (2 *b2*, *a1*)
- S^2 = 0.95
- SOMO = a_2</td></tr>
<tr><td>SCS-MP2</td><td colspan="3">- Planar geometry
- 4 imaginary frequencies (3 *b2*, *a2*)
- S^2 = 0.78
- SOMO = a_1</td></tr>
</table>

Table S3: Vertical excitation energies as relative energy differences in eV calculated for the MS-SA-CASPT2(9,10)/cc-pVDZ optimized geometries of the twisted X⁺ ^{2}A (1 ^{2}A$_2$) state of the ortho-benzyne cation, optimized at the CASPT2(9,10)/cc-pVDZ level of theory. All methods employ the cc-pVQZ basis set. In all cases, the ground state is the X⁺ ^{2}A (1 ^{2}A$_2$) state. All values in [eV].

Vertical excitation from equilibrium geometry of 1 ^{2}A (1 ^{2}A$_2$) state		
	First excited state (1 ^{2}B)	Second excited state (2 ^{2}A)
wB97xD	0.97	1.07
B3LYP	0.86	0.75
M06-2X	1.00	1.22
CC2	1.08	1.37
SCS-CC2	1.13	1.35
ADC(2)	1.06	1.20
SCS-ADC(2)	1.13	1.35
SA-UNO-CAS(11,14)	1.21	2.43
SA-UNO-CAS(11,14) + MS-PT2	0.60	1.32
MS-SA-CASPT2(11,14)	0.77	1.14

Table S4: Vertical excitation energies as relative energy differences in eV calculated for the MS-SA-CASPT2(9,10)/cc-pVDZ optimized geometries of the planar 1 ^{2}B (1 ^{2}B$_1$) state of the o-benzyne cation, optimized at the CASPT2(9,10)/cc-pVDZ level of theory. All methods employ the cc-pVQZ basis set. All values in [eV].

Vertical excitation from equilibrium geometry of 1 ^{2}B (1 ^{2}B$_1$) state			
	Ground state	First excited state	Second excited state
wB97xD	^{2}A$_1$	0.16 (1 ^{2}B)	0.64 (2 ^{2}A)
B3LYP	^{2}B$_1$	-0.22 (2 ^{2}B)	0.19 (3 ^{2}B)
M06-2X	^{2}A$_1$	0.16 (1 ^{2}B)	0.16 (2 ^{2}A)
CC2	^{2}A$_1$	-0.18 (1 ^{2}B)	0.19 (2 ^{2}A)
SCS-CC2	^{2}A$_1$	-0.18 (1 ^{2}B)	0.17 (2 ^{2}A)
ADC(2)	^{2}A$_1$	-0.31 (1 ^{2}B)	0.09 (2 ^{2}A)
SCS-ADC(2)	^{2}A$_1$	-0.30 (1 ^{2}B)	0.09 (2 ^{2}A)
SA-UNO-CAS(11,14)	^{2}B$_1$	1.16 (1 ^{2}A)	3.70 (2 ^{2}B)
SA-UNO-CAS(11,14) + MS-PT2	^{2}B$_1$	0.30 (1 ^{2}A)	2.72 (2 ^{2}B)
MS-SA-CASPT2(11,14)	^{2}B$_1$	0.34 (1 ^{2}A)	0.42 (2 ^{2}A)

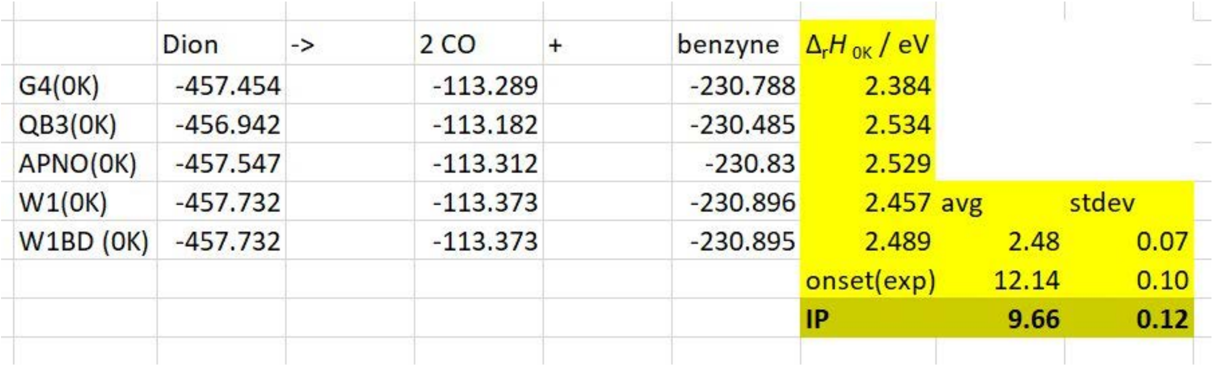
Table S5: Vertical excitation energies as relative energy differences in eV calculated via MS-SA-CASPT2(9,10)/cc-pVDZ of the ortho-benzyne cation at the equilibrium geometry of the 1 $^1A_1$ neutral o-benzyne, optimized at the CASPT2(10,10)/cc-pVDZ level of theory. All methods employ the cc-pVQZ basis set. In all cases, the ground state is the X^+ ^2A (1 $^2A_2$) state. All values in [eV].

Vertical excitation of the cation from the equilibrium geometry of 1 ^1A (1 $^1A_1$) state of the neutral molecule		
	First excited state (1 ^2B)	Second excited state (2 ^2A)
wB97xD	0.31	0.33
B3LYP	0.04	0.08
M06-2X	0.10	0.42
CC2	-0.03	-0.07
SCS-CC2	-0.02	-0.10
ADC(2)	-0.17	-0.18
SCS-ADC(2)	-0.15	-0.20
SA-UNO-CAS(11,14)	0.55	-3.51
SA-UNO-CAS(11,14) + MS-PT2	0.16	1.83
MS-SA-CASPT2(11,14)	0.00	0.36

Table S6: Vertical ionisation energies at the geometry of neutral ortho-benzyne as a function of computational method. For all methods Dunning's cc-pVQZ basis set was used. For the reference values (assumed to be CASPT2(11,14)/cc-pVQZ) see the main article.

Method	wB97xD	M062X	B3LYP	CC2	SCS-CC2	SCS-MP2	MP2	UNO-CAS + PT2
IE_{vert} /eV	9.59	9.69	9.61	10.18	10.15	10.24	10.29	10.16

Table S7: Adiabatic ionization energy derived by a thermochemical cycle. The heat of reaction $\Delta_R H$ (0K) for benzocyclobutenedione → ortho-benzyne + 2 CO was computed by various methods. The value was then subtracted from the appearance energy $AE_{0K}(C_8H_4O_2, C_6H_4^+)$ = 12.14 eV obtained from the breakdown diagram given in Figure 6.



	Dion	->	2 CO	+	benzyne	$\Delta_r H_{0K}$ / eV		
G4(0K)	-457.454		-113.289		-230.788	2.384		
QB3(0K)	-456.942		-113.182		-230.485	2.534		
APNO(0K)	-457.547		-113.312		-230.83	2.529		
W1(0K)	-457.732		-113.373		-230.896	2.457	avg	stdev
W1BD (0K)	-457.732		-113.373		-230.895	2.489	2.48	0.07
						onset(exp)	12.14	0.10
						IP	**9.66**	**0.12**

Table S8: Cartesian coordinates for the 1 $^1A_1$ equilibrium geometry of the neutral ortho-benzyne obtained at the CASPT2(10,10)/cc-pVDZ level of theory. The geometry was verified as a true minimum by a numerical CASPT2(10,10)/cc-pVDZ hessian calculation.

	X in Å	Y in Å	Z in Å
C	0.6402	0.000	-1.5529
C	-0.6402	0.000	-1.5529
C	1.4695	0.000	-0.4268
C	-1.4695	0.000	-0.4268
C	-0.7091	0.000	0.7718
C	0.7091	0.000	0.7718
H	1.2362	0.000	1.7323
H	-1.2362	0.000	1.7323
H	-2.5621	0.000	-0.4258
H	2.5621	0.000	-0.4258

Table S9: Cartesian coordinates for the 1 ^2B (1 $^2B_1$) equilibrium geometry of the ortho-benzyne cation obtained at the CASPT2(9,10)/cc-pVDZ level of theory. The geometry was verified as a true minimum by a numerical CASPT2(9,10)/cc-pVDZ hessian calculation.

	X in Å	Y in Å	Z in Å
C	0.6525	0.0001	-1.5223
C	-0.6525	-0.0001	-1.5223
C	1.5157	-0.0001	-0.4278
C	-1.5157	0.0001	-0.4278
C	-0.7406	0.0001	0.7568
C	0.7406	-0.0001	0.7568
H	1.2408	0.0005	1.7326
H	-1.2408	-0.0005	1.7326
H	-2.6063	-0.0002	-0.4408
H	2.6063	0.0002	-0.4408

Table S10: Cartesian coordinates for the 1 ^2A (1 $^2A_2$) equilibrium geometry of the o-benzyne cation obtained at the CASPT2(9,10)/cc-pVDZ level of theory. The geometry was verified as a true minimum by a numerical CASPT2(9,10)/cc-pVDZ hessian calculation.

	X in Å	Y in Å	Z in Å
C	0.6261	-0.1289	-1.5747
C	-0.6261	0.1289	-1.5747
C	1.4493	-0.0471	-0.4368
C	-1.4493	0.0471	-0.4368

C	-0.6941	0.0559	0.8095
C	0.6941	-0.0559	0.8095
H	1.2466	-0.0704	1.7532
H	-1.2466	0.0704	1.7532
H	-2.5334	-0.1087	-0.4527
H	2.5334	0.1087	-0.4527

Table S11: Cartesian coordinates for the 2 ^{2}A (1 $^2A_1$) equilibrium geometry of the o-benzyne cation obtained at the CASPT2(9,10)/cc-pVDZ level of theory. The geometry was verified as a true minimum by a numerical SA-MS-CASPT2(9,10)/cc-pVDZ hessian calculation.

	X in Å	Y in Å	Z in Å
C	0.6594	0.0000	-1.5026
C	-0.6594	0.0000	-1.5026
C	1.5149	0.0000	-0.4287
C	-1.5149	0.0000	-0.4287
C	-0.7010	0.0000	0.7565
C	0.7010	0.0000	0.7565
H	1.2423	0.0000	1.7097
H	-1.2423	0.0000	1.7097
H	-2.6070	0.0000	-0.4365
H	2.6070	0.0000	-0.4365

Table S12: Cartesian coordinates for the 2 ^{2}B equilibrium geometry of the o-benzyne cation obtained at the SA-MS-CASPT2(9,10)/cc-pVDZ level of theory. The geometry was verified as a true minimum by a numerical SA-MS-CASPT2(9,10)/cc-pVDZ Hessian calculation.

	X in Å	Y in Å	Z in Å
C	0.6243	-0.1383	-1.5751
C	-0.6272	0.1321	-1.5779
C	1.4479	-0.0495	-0.4304
C	-1.4454	0.0498	-0.4341
C	-0.6948	0.0595	0.8012
C	0.6965	-0.0560	0.8064
H	1.2431	-0.0770	1.7548
H	-1.2441	0.0718	1.7488
H	-2.5305	-0.1102	-0.4451
H	2.5302	0.1178	-0.4516

Table S13: Cartesian coordinates for the saddle point identified on the potential energy surface of the 1 ^{2}B (1 $^2B_1$) state of the ortho-benzyne cation, obtained at the CASPT2(9,10)/cc-pVDZ level of theory. The geometry was verified as a first order saddle point by a numerical MS-SA-CASPT2(9,10)/cc-pVDZ hessian calculation.

	X in Å	Y in Å	Z in Å
C	-0.1071	-1.3222	0.0000
C	-1.2633	-0.6884	0.0000
C	1.1986	-0.9712	0.0000
C	-1.3262	0.6984	0.0000
C	-0.0127	1.2564	0.0000
C	1.1599	0.4818	0.0000
H	2.1467	0.9586	0.0000
H	0.0761	2.3473	0.0000
H	-2.2487	1.2854	0.0000
H	2.1130	-1.5667	0.0000

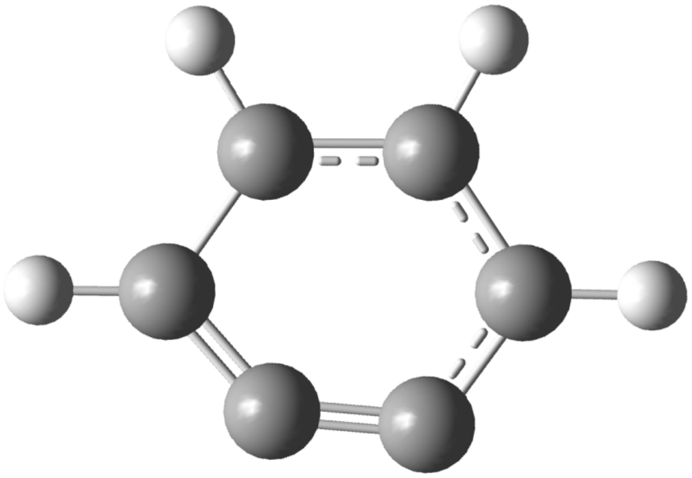


Table S14: Vertical (IE_{vert}) and adiabatic (IE_{ad}) ionisation energies of **1** as well as IE_{ad} including zero point vibrational energy, obtained from a basis-set-limit extrapolation using cc-pVQZ and cc-pV5Z results.[2]

	1 ^{2}A **(1 $^2A_2$)**	**2 ^{2}A** **(1 $^2A_1$)**	**1 ^{2}B** **(1 $^2B_1$)**	**2 ^{2}B**
IE_{vert}	9.80 eV	10.16 eV	9.85 eV	12.03 eV
IE_{ad}	9.65 eV	10.09 eV	9.81 eV	11.99 eV
IE_{ad} (ZPE)	9.60 eV	10.12 eV	9.73 eV	12.03 eV

Table S15: Comparison of experimentally reported ionization energies. With the exception of the present work all values correspond to vertical IE.

Source	Method	IE /eV
Fisher & Lossing, 1963 [3]	MS	9.5
Grützmacher et al, 1967 [4]	MS	9.5
Genzel & Osberghaus, 1967 [5]	MS	9.5
Cited via [6]		
Dewar and Tien, 1985 [7]	PES	9.24
		9.75
		9.87
Schulz & Schweig, 1988 [8]	PES	9.23
Cited via [6]		9.41
		9.70
Guo & Grabowski, 1991 [9]	Ion-molecule rxn/ thermochemical cycle	9.03
Zhang and Chen, 1992 [10]	PES	9.03
		9.77
Werstiuk et al, 1995 [11]	PES	9.7
Chrostowska et al, 2010 [6]	PES	9.65
This work	TPES	9.51 (X ^{2}A)
		9.64 (1 ^{2}B)
		9.89 (2 ^{2}A)

MS=Mass Spectrometry, PES=Photoelectron Spectroscopy, TPES=Threshold PES

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