Electronic Supplementary Material for PCCP

Supplementary data

Table S1. Cartesian coordinates (in Å) of all the atoms in the CASPT2(11,12) optimized geometries for the ground (1^2B_1) and first excited (1^2A_2) states of the *o*-benzyne radical cation (for notations, see Figure 1), together with the CASSCF(7,8) frequencies (in cm^{-1}) (at the CASSCF(7,8) optimized geometries).

o-$C_6H_4^+$	1^2B_1			1^2A_2		
	X	Y	Z	X	Y	Z
C_1	0.0000	0.6424	-1.2007	0.0000	0.6256	-1.2705
C_2	0.0000	1.4990	-0.1356	0.0000	1.4453	-0.1394
C_3	0.0000	0.7314	1.0422	0.0000	0.6864	1.0900
C_4	0.0000	-0.7314	1.0422	0.0000	-0.6864	1.0900
C_5	0.0000	-1.4990	-0.1356	0.0000	-1.4453	-0.1394
C_6	0.0000	-0.6424	-1.2007	0.0000	-0.6256	-1.2705
H_1	0.0000	2.5707	-0.1435	0.0000	2.5206	-0.1371
H_2	0.0000	1.2226	2.0014	0.0000	1.2251	2.0207
H_3	0.0000	-1.2226	2.0014	0.0000	-1.2251	2.0207
H_4	0.0000	-2.5707	-0.1435	0.0000	-2.5206	-0.1371

o-$C_6H_4^+$	Symmetry	Freq.					
1^2B_1	a_1	633.5	968.9	1092.7	1252.9	1441.4	1549.9
		1900.1	3359.9	3403.2			
	a_2	407.1	570.7	922.1	1036.5		
	b_2	i875.16	632.5	971.1	1230.3	1393.2	1559.6
		3348.5	3400.6				
	b_1	363.8	740.9	998.3			
1^2A_2	a_1	624.6	1024.9	1098.7	1276.4	1464.1	1640.4
		2010.0	3369.9	3384.5			
	a_2	361.6	480.6	918.2	1054.6		
	b_2	454.9	862.1	1031.2	1195.7	1427.5	1515.5
		3356.2	3378.4				
	b_1	320.6	799.5	1017.1			

Table S2. Cartesian coordinates (in Å) of all the atoms in the CASPT2(11,12) optimized geometries for the ground (1^2A_2) and first excited (1^2A_1) states of the *m*-benzyne radical cation (for notations, see Figure 1), together with the CASSCF(7,8) frequencies (in cm^{-1}) (at the CASSCF(7,8) optimized geometries).

m-$C_6H_4^+$	1^2A_2			1^2A_1		
	X	Y	Z	X	Y	Z
C_1	0.0000	0.0000	1.8143	0.0000	0.0000	1.6473
C_2	0.7094	0.0000	0.6618	0.9620	0.0000	0.6923
C_3	1.1595	0.0000	-0.6969	1.1991	0.0000	-0.6346
C_4	0.0000	0.0000	-1.4935	0.0000	0.0000	-1.3721
C_5	-1.1595	0.0000	-0.6969	-1.1991	0.0000	-0.6346
C_6	-0.7094	0.0000	0.6618	-0.9620	0.0000	0.6923
H_1	0.0000	0.0000	2.8873	0.0000	0.0000	2.7202
H_2	2.1790	0.0000	-1.0299	2.1783	0.0000	-1.0761
H_3	0.0000	0.0000	-2.5678	0.0000	0.0000	-2.4484
H_4	-2.1790	0.0000	-1.0299	-2.1783	0.0000	-1.0761

m-$C_6H_4^+$	Symmetry	Freq.					
1^2A_1	a_1	569.1	898.1	1087.1	1132.9	1502.9	1786.1
		3360.7	3386.0	3408.5			
	a_2	581.2	1818.6				
	b_2	243.1	920.7	1139.7	1181.2	1302.3	1383.2
		1587.4	3381.3				
	b_1	194.4	264.5	546.9	773.3	1008.2	
1^2A_2	a_1	852.9	910.9	1052.5	1142.8	1502.2	1863.7
		3381.1	3416.1	3420.2			
	a_2	551.5	824.3				
	b_2	572.7	877.6	1066.4	1187.7	1351.6	1451.7
		1558.0	3412.3				
	b_1	284.8	522.1	788.9	883.4	1006.8	

Table S3. Cartesian coordinates (in Å) of all the atoms in the CASPT2(7,8) optimized geometry for the ground (1^2B_{1u}) state of the *p*-benzyne radical cation (for notations, see Figure 1), together with the CASSCF(7,8) frequencies (in cm^{-1}) (at the CASSCF(7,8) optimized geometry).

p-$C_6H_4^+$		1^2B_{1u}	
	X	Y	Z
C_1	0.0000	0.0000	1.2373
C_2	0.0000	1.2343	0.7343
C_3	0.0000	1.2343	-0.7343
C_4	0.0000	0.0000	-1.2373
C_5	0.0000	-1.2343	-0.7343
C_6	0.0000	-1.2343	0.7343
H_1	0.0000	2.1911	1.2246
H_2	0.0000	2.1911	-1.2246
H_3	0.0000	-2.1911	-1.2246
H_4	0.0000	-2.1911	1.2246

p-$C_6H_4^+$	Symmetry	Freq.				
1^2B_{1u}	a_g	765.5	1045.9	1181.9	1389.6	3388.7
	a_u	443.0	944.7			
	b_{1g}	1900.8				
	b_{2g}	i2123.25	900.2			
	b_{3g}	530.0	1330.2	1787.8	3371.4	
	b_{1u}	1089.4	1476.6	1807.8	3374.9	
	b_{2u}	967.6	1156.2	1500.1	3385.3	
	b_{3u}	221.5	760.2			

Table S4. The important configurations [a] in the CASSCF(7,8) wavefunctions for the ground and excited states of the *o*-, *m*-, and *p*-benzyne radical cations calculated at the CASPT2(7,8) optimized geometries. The important configurations in the CASSCF(8,8) wavefunctions [b] for the ground states (S_0) of the *o*-, *m*-, and *p*-benzynes are also given in the table.

	State	Important configurations (coefficients)	
o-$C_6H_4^+$ (C_{2v})	1^1A_1 (S_0, *o*-C_6H_4)	$...(1b_1)^2(10a_1)^2(1a_2)^2(2b_1)^2$	(0.90)
		$...(1b_1)^2(10a_1)^0(1a_2)^2(2b_1)^2(8b_2)^2$	(0.25)
	1^2A_1	$...(1b_1)^2(10a_1)^1(1a_2)^2(2b_1)^2$	(0.93)
	1^2A_2	$...(1b_1)^2(10a_1)^2(1a_2)^1(2b_1)^2$	(0.91)
		$...(1b_1)^2(10a_1)^0(1a_2)^1(2b_1)^2(8b_2)^2$	(0.26)
	1^2B_1(X)	$...(1b_1)^2(10a_1)^2(1a_2)^2(2b_1)^1$	(0.90)
		$...(1b_1)^2(10a_1)^0(1a_2)^2(2b_1)^1(8b_2)^2$	(0.27)
	1^2B_2	$...(1b_1)^2(10a_1)^0(1a_2)^2(2b_1)^2(8b_2)^1$	(0.86)
		$...(1b_1)^2(10a_1)^2(1a_2)^2(2b_1)^0(8b_2)^1$	(0.27)
		$...(1b_1)^2(10a_1)^1(1a_2)^2(2b_1)^1(8b_2)^0(2a_2)^1$	(0.21)
m-$C_6H_4^+$ (C_{2v})	1^1A_1(S_0, *m*-C_6H_4)	$...(1b_1)^2(2b_1)^2(1a_2)^2(11a_1)^2$	(0.88)
		$...(1b_1)^2(2b_1)^2(1a_2)^2(11a_1)^0(7b_2)^2$	(0.32)
	1^2A_1	$...(1b_1)^2(2b_1)^2(1a_2)^2(11a_1)^1$	(0.93)
	1^2A_2(X)	$...(1b_1)^2(2b_1)^2(1a_2)^1(11a_1)^2$	(0.94)
	1^2B_1	$...(1b_1)^2(2b_1)^1(1a_2)^2(11a_1)^2$	(0.85)
		$...(1b_1)^2(2b_1)^1(1a_2)^2(11a_1)^0(7b_2)^2$	(0.39)
	1^2B_2	$...(1b_1)^2(2b_1)^2(1a_2)^0(11a_1)^2(7b_2)^1$	(0.91)
p-$C_6H_4^+$ (D_{2h})	1^1A_g (S_0, *p*-C_6H_4)	$..(1b_{3u})^2(1b_{2g})^2(1b_{1g})^2(5b_{1u})^2$	(0.75)
		$...(1b_{3u})^2(1b_{2g})^2(1b_{1g})^2(5b_{1u})^0(6a_g)^2$	(0.54)
	1^2A_g	$..(1b_{3u})^2(1b_{2g})^2(1b_{1g})^2(5b_{1u})^0(6a_g)^1$	(0.92)
	1^2A_u	$..(1b_{3u})^2(1b_{2g})^2(1b_{1g})^d(5b_{1u})^u(6a_g)^u$	(0.81)
		$..(1b_{3u})^2(1b_{2g})^2(1b_{1g})^u(5b_{1u})^d(6a_g)^u$	(0.47)
	1^2B_{1g}	$..(1b_{3u})^2(1b_{2g})^2(1b_{1g})^1(5b_{1u})^2$	(0.75)
		$..(1b_{3u})^2(1b_{2g})^2(1b_{1g})^1(5b_{1u})^0(6a_g)^2$	(0.52)
	1^2B_{1u}(X)	$..(1b_{3u})^2(1b_{2g})^2(1b_{1g})^2(5b_{1u})^1$	(0.92)
	1^2B_{2g}	$..(1b_{3u})^2(1b_{2g})^1(1b_{1g})^2(5b_{1u})^2$	(0.73)
		$..(1b_{3u})^2(1b_{2g})^1(1b_{1g})^2(5b_{1u})^0(6a_g)^2$	(0.58)
	1^2B_{2u}	$..(1b_{3u})^2(1b_{2g})^u(1b_{1g})^u(5b_{1u})^d(6a_g)^2$	(0.76)
		$..(1b_{3u})^u(1b_{2g})^2(1b_{1g})^d(5b_{1u})^2(6a_g)^u$	(0.35)
		$..(1b_{3u})^2(1b_{2g})^u(1b_{1g})^d(5b_{1u})^u(6a_g)^2$	(0.29)
	1^2B_{3g}	$...(1b_{3u})^2(1b_{2g})^u(1b_{1g})^d(5b_{1u})^2(6a_g)^u$	(0.62)
		$...(1b_{3u})^2(1b_{2g})^d(1b_{1g})^u(5b_{1u})^2(6a_g)^u$	(0.59)
		$...(1b_{3u})^u(1b_{2g})^2(1b_{1g})^u(5b_{1u})^d(6a_g)^2$	(0.30)
	1^2B_{3u}	$..(1b_{3u})^2(1b_{2g})^d(1b_{1g})^2(5b_{1u})^u(6a_g)^u$	(0.81)
		$..(1b_{3u})^2(1b_{2g})^u(1b_{1g})^2(5b_{1u})^d(6a_g)^u$	(0.46)

[a] The configurations with coefficients (absolute values) larger than 0.20.

[b] Ref.13.

Table S5. Mulliken spin (S) and LoProp charge (Q) populations in the 1^2B_1 (X) and 1^2A_2 states of the *o*-benzyne radical cation obtained in the CASSCF(11,12)//CASPT2(11,12) calculations. In Table we also give the charge populations in the ground state (S_0) of the *o*-benzyne molecule obtained in the CASSCF(12,12)//CASPT2(12,12) calculations.

		C_1	C_2	C_3	H_1	H_2
1^2B_1	S	0.261	-0.080	0.315	-0.001	0.005
	Q	0.171	-0.081	0.037	0.190	0.183
1^2A_2	S	0.035	0.426	0.031	0.007	0.001
	Q	0.068	0.105	-0.049	0.196	0.180
S_0	Q	-0.019	-0.115	-0.131	0.136	0.128

Table S6. Mulliken spin (S) and LoProp charge (Q) populations in the 1^2A_2 (X) and 1^2A_1 states of the *m*-benzyne radical cation obtained in the CASSCF(11,12)//CASPT2(11,12) calculations. In Table we also give the charge populations in the ground state (S_0) of the *m*-benzyne molecule obtained in the CASSCF(12,12)//CASPT2(12,12) calculations.

		C_1	C_2	C_3	C_4	H_1	H_2	H_3
1^2A_2	S	-0.016	0.122	0.448	-0.141	0.000	0.008	0.000
	Q	0.076	0.138	-0.035	-0.050	0.215	0.190	0.175
1^2A_1	S	-0.003	0.479	-0.033	0.073	0.009	0.005	0.020
	Q	-0.065	0.247	-0.113	-0.020	0.227	0.206	0.178
S_0	Q	-0.123	-0.014	-0.158	-0.090	0.152	0.142	0.123

Table S7. Mulliken spin (S) and LoProp charge (Q) populations in the 1^2B_{1u} (X) state of the *p*-benzyne radical cation obtained in the CASSCF(7,8)//CASPT2(7,8) calculations. In Table we also give the charge populations in the ground state (S_0) of the *p*-benzyne molecule obtained in the CASSCF(8,8)//CASPT2(8,8) calculations.

		C_1	C_2	H_1
1^2B_{1u}	S	0.458	0.019	0.002
	Q	0.242	-0.086	0.215
S_0	Q	-0.007	-0.138	0.142

Table S 8. Isotropic ^{13}C hyperfine coupling constants ($a(C_i)$, in Gauss) in the ground (X) and first excited states of the *o*- and *m*-benzyne radical cations and in the ground (X) state of the *p*-benzyne radical cation, obtained in the UB3LYP calculations [a] with the 6-31G(d,p) (B1) and 6-311G(d,p) (B2) basis sets (for atom lablels, see Figure 1). The $<S^2>$ values in the UB3LYP calculations are also given in the table.

	State	Basis	*a* (C_1)	*a* (C_2)	*a* (C_3)	*a* (C_4)	$<S^2>$
o-$C_6H_4^+$	1^2B_1 (X)	B1	9.4	-7.9	13.3	13.3	0.767
		B2	3.6	-7.4	5.2	5.2	0.767
	1^2A_2	B1	-5.8	20.0	-1.6	-1.6	0.765
		B2	-8.0	9.4	-3.4	-3.4	0.764
m-$C_6H_4^+$	1^2A_2 (X)	B1	-3.3	1.5	21.1	-12.4	0.769
		B2	-3.5	-3.8	11.0	-11.7	0.768
	1^2A_1	B1	-12.4	70.9	-5.3	40.7	0.765
		B2	-9.6	71.8	-4.2	43.7	0.764
p-$C_6H_4^+$	1^2B_{1u} (X)	B1	61.3	29.9	29.9	61.3	0.773
		B2	60.4	34.8	34.8	60.4	0.772

[a] The UB3LYP calculations were performed at the CASPT2(11,12) optimized geometries for the ground and first excited states of the *o*- and *m*-$C_6H_4^+$ cations and at the CASPT2(7,8) optimized geometry for the ground state of the *p*-$C_6H_4^+$ cation.

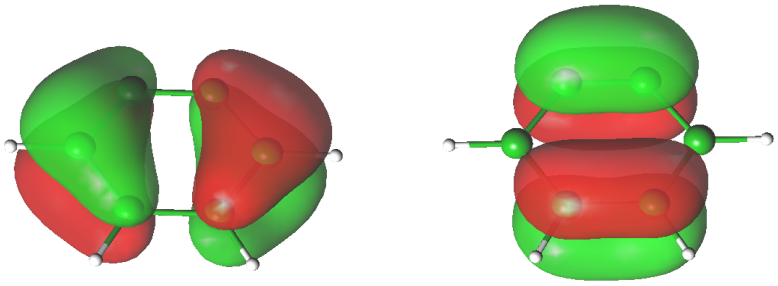
Table S9. The NICS (nucleus-independent chemical shift) values in the ground (X) and first excited states of the *o*- and *m*-benzyne radical cations and in the ground (X) state of the *p*-benzyne radical cation, obtained in the UB3LYP calculations [a] with the 6-31G(d,p) and 6-311G(d,p) basis sets

Molecule	State	UB3LYP/ 6-31G(d,p)	UB3LYP/6-311G(d,p)
o-C_6H_4+	1^2B_1(X)	8.3	9.2
o-C_6H_4+	1^2A_2	26.0	24.6
m-C_6H_4+	1^2A_2(X)	0.1	-0.1
m-C_6H_4+	1^2A_1	-22.0	-21.5
p-C_6H_4+	1^2B_{1u}(X)	-28.4	-27.8

[a] The UB3LYP calculations were performed at the CASPT2(11,12) optimized geometries for the ground and first excited states of the *o*- and *m*-$C_6H_4^+$ cations and at the CASPT2(7,8) optimized geometry for the ground state of the *p*-$C_6H_4^+$ cation. The NICS values were calculated at the central points of the carbon-frameworks.

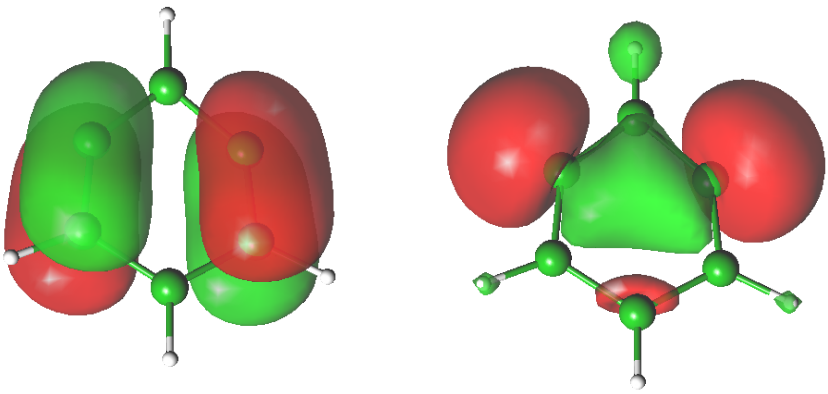
Electronic Supplementary Material for PCCP

1. The drawings of the $1a_2$ and $2b_1$ orbitals of the *o*-benzyne molecule:



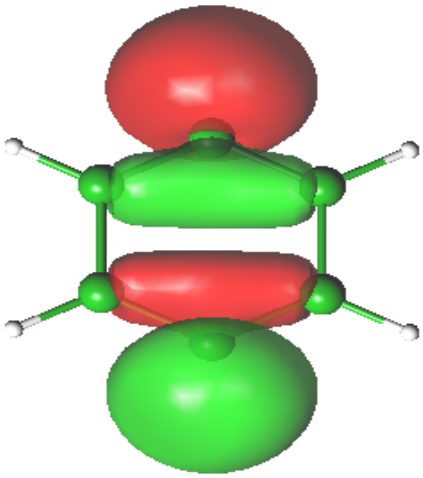
$1a_2$ $2b_1$

2. The drawings of the $1a_2$ and $11a_1$ orbitals of the *m*-benzyne molecule:



$1a_2$ $11a_1$

3. The drawing of the $5b_{1u}$ orbital of the *p*-benzyne molecule:



$5b_{1u}$