Supporting information for:

Free Cyclooctatetraene Dianion: Planarity, Aromaticity, and Theoretical Challenges

Alexander Yu. Sokolov,* D. Brandon Magers, Judy I. Wu, Wesley D. Allen,*

Paul v. R. Schleyer, and Henry F. Schaefer III

Center for Computational Quantum Chemistry, The University of Georgia, Athens, GA, 30602

E-mail: alex@ccqc.uga.edu; wdallen@uga.edu

*To whom correspondence should be addressed

Table S1: Cartesian coordinates (a.u.) of the neutral cyclooctatetraene structure (C_8H_8, D_{2d} symmetry) optimized at the AE-CCSD(T)/aug(H)-cc-pCVTZ level of theory.

1	C	2.923583	-1.267862	0.752189
2	C	2.923583	1.267862	0.752189
3	C	-2.923583	1.267862	0.752189
4	C	-2.923583	-1.267862	0.752189
5	C	1.267862	2.923583	-0.752189
6	C	-1.267862	2.923583	-0.752189
7	C	-1.267862	-2.923583	-0.752189
8	C	1.267862	-2.923583	-0.752189
9	H	4.366062	-2.221279	1.858125
10	H	4.366062	2.221279	1.858125
11	H	-4.366062	2.221279	1.858125
12	H	-4.366062	-2.221279	1.858125
13	H	2.221279	4.366062	-1.858125
14	H	-2.221279	4.366062	-1.858125
15	H	-2.221279	-4.366062	-1.858125
16	H	2.221279	-4.366062	-1.858125

Table S2: Cartesian coordinates (a.u.) of the cyclooctatetraene dianion structure ($C_8H_8^{2-}$, D_{8h} symmetry) optimized at the AE-CCSD(T)/aug(H)-cc-pCVTZ level of theory.

1	C	0.000000	-3.495824	0.000000
2	C	-2.471921	-2.471921	0.000000
3	C	0.000000	3.495824	0.000000
4	C	2.471921	2.471921	0.000000
5	C	-3.495824	0.000000	0.000000
6	C	-2.471921	2.471921	0.000000
7	C	3.495824	0.000000	0.000000
8	C	2.471921	-2.471920	0.000000
9	H	0.000000	-5.565273	0.000000
10	H	-3.935243	-3.935243	0.000000
11	H	0.000000	5.565273	0.000000
12	H	3.935243	3.935243	0.000000
13	H	-5.565273	0.000000	0.000000
14	H	-3.935243	3.935243	0.000000
15	H	5.565273	0.000000	0.000000
16	H	3.935243	-3.935243	0.000000

Table S3: Cartesian coordinates (a.u.) of the $Na_2C_8H_8$ structure (D_{8h} symmetry) optimized at the AE-CCSD(T)/aug(H,Na)-cc-pCVTZ level of theory.

1	NA	0.000000	0.000000	3.426177
2	NA	0.000000	0.000000	-3.426177
3	C	0.000000	-3.506576	0.000000
4	C	-2.479523	-2.479523	0.000000
5	C	0.000000	3.506576	0.000000
6	C	2.479523	2.479523	0.000000
7	C	-3.506576	0.000000	0.000000
8	C	-2.479523	2.479523	0.000000
9	C	3.506576	0.000000	0.000000
10	C	2.479523	-2.479523	0.000000
11	H	0.000000	-5.555251	0.000000
12	H	-3.928155	-3.928155	0.000000
13	H	0.000000	5.555251	0.000000
14	H	3.928155	3.928155	0.000000
15	H	-5.555251	0.000000	0.000000
16	H	-3.928155	3.928155	0.000000
17	H	5.555251	0.000000	0.000000
18	H	3.928155	-3.928155	0.000000

Table S4: Harmonic vibrational frequencies (ω_e, cm^{-1}) and corresponding infrared intensities (km mol^{-1}) of the neutral cyclooctatetraene C_8H_8 computed at the AE-CCSD(T)/aug(H)-cc-pCVTZ level of theory.

Mode	Description	ω_e	Intensity
$\omega_1(a_1)$	C–H stretch	3139	0.0
$\omega_2(a_1)$	C–C stretch	1716	0.0
$\omega_3(a_1)$	bend	1249	0.0
$\omega_4(a_1)$	bend	905	0.0
$\omega_5(a_1)$	C–C stretch	788	0.0
$\omega_6(a_1)$	bend	197	0.0
$\omega_7(a_2)$	C–H stretch	3089	0.0
$\omega_8(a_2)$	bend	1394	0.0
$\omega_9(a_2)$	bend	1005	0.0
$\omega_{10}(a_2)$	bend	934	0.0
$\omega_{11}(a_2)$	bend	243	0.0
$\omega_{12}(b_1)$	C–H stretch	3101	0.0
$\omega_{13}(b_1)$	C–C stretch	1483	0.0
$\omega_{14}(b_1)$	C–C stretch	1047	0.0
$\omega_{15}(b_1)$	bend	986	0.0
$\omega_{16}(b_1)$	bend	666	0.0
$\omega_{17}(b_1)$	bend	251	0.0
$\omega_{18}(b_2)$	C–H stretch	3125	29.9
$\omega_{19}(b_2)$	C–C stretch	1683	1.5
$\omega_{20}(b_2)$	C–C stretch	1241	0.6
$\omega_{21}(b_2)$	bend	714	82.5
$\omega_{22}(b_2)$	bend	296	0.8
$\omega_{23}(e)$	C–H stretch	3131	50.9
$\omega_{24}(e)$	C–H stretch	3097	1.6
$\omega_{25}(e)$	C–C stretch	1692	1.7
$\omega_{26}(e)$	C–C stretch	1445	0.0
$\omega_{27}(e)$	bend	1259	1.5
$\omega_{28}(e)$	bend	1006	0.3
$\omega_{29}(e)$	C–C stretch	968	3.0
$\omega_{30}(e)$	bend	827	22.6
$\omega_{31}(e)$	bend	651	15.4
$\omega_{32}(e)$	bend	383	1.2

Table S5: Harmonic vibrational frequencies (ω_e, cm^{-1}) and corresponding infrared intensities (km mol^{-1}) of the $Na_2C_8H_8$ structure computed at the AE-CCSD/aug(H,Na)-cc-pCVDZ level of theory.

Mode	Description	ω_e	Intensity
$\omega_1(a_{1g})$	C–H stretch	3219	0.0
$\omega_2(a_{1g})$	C–C stretch	755	0.0
$\omega_3(a_{1g})$	sym. perpendicular disp. of Na	230	0.0
$\omega_4(a_{2g})$	in-plane bend	1392	0.0
$\omega_5(b_{1g})$	C–H stretch	3172	0.0
$\omega_6(b_{1g})$	in-plane bend	998	0.0
$\omega_7(b_{2g})$	C–C stretch	1668	0.0
$\omega_8(b_{2g})$	in-plane bend	1303	0.0
$\omega_9(e_{1g})$	out-of-plane bend	737	0.0
$\omega_{10}(e_{1g})$	asym. parallel disp. of Na	189	0.0
$\omega_{11}(e_{2g})$	C–H stretch	3192	0.0
$\omega_{12}(e_{2g})$	C–C stretch	1529	0.0
$\omega_{13}(e_{2g})$	C–C stretch	1180	0.0
$\omega_{14}(e_{2g})$	in-plane bend	336	0.0
$\omega_{15}(e_{3g})$	out-of-plane bend	858	0.0
$\omega_{16}(e_{3g})$	out-of-plane bend	487	0.0
$\omega_{17}(a_{2u})$	umbrella motion	694	214.7
$\omega_{18}(a_{2u})$	asym. perpendicular disp. of Na	258	83.7
$\omega_{19}(b_{2u})$	out-of-plane bend	912	0.0
$\omega_{20}(b_{2u})$	out-of-plane bend	489	0.0
$\omega_{21}(e_{1u})$	C–H stretch	3209	78.9
$\omega_{22}(e_{1u})$	in-plane bend	1450	5.0
$\omega_{23}(e_{1u})$	C–C stretch	903	38.5
$\omega_{24}(e_{1u})$	sym. parallel disp. of Na	172	17.3
$\omega_{25}(e_{2u})$	out-of-plane bend	774	0.0
$\omega_{26}(e_{2u})$	out-of-plane bend	191	0.0
$\omega_{27}(e_{3u})$	C–H stretch	3177	0.0
$\omega_{28}(e_{3u})$	C–C stretch	1476	0.0
$\omega_{29}(e_{3u})$	C–C stretch	1307	0.0
$\omega_{30}(e_{3u})$	in-plane bend	776	0.0