Supporting Information

The Electronic States of a Double Carbon Vacancy Defect in Pyrene: A Model Study for Graphene

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State	CASSCF	MRCI	MRCI+Q	B3-LYP	Config.[a,b]
^1A_g	0.000[c]	0.000[c]	0.000[c]	0.000[c]	$12a_g^2 3b_{3u}^0 10b_{2u}^0 2b_{1g}^2 11b_{1u}^2 2b_{2g}^2 9b_{3g}^0 2a_u^0$ (54%)
$^3B_{3g}$	1.607	1.635	1.646	1.616	$12a_g^2 3b_{3u}^0 10b_{2u}^1 2b_{1g}^2 11b_{1u}^1 2b_{2g}^2 9b_{3g}^0 2a_u^0$ (41%)
$^3B_{2u}$	1.741	1.799	1.827	2.378	$12a_g^2 3b_{3u}^0 10b_{2u}^0 2b_{1g}^2 11b_{1u}^1 2b_{2g}^2 9b_{3g}^1 2a_u^0$ (31%)
$^3B_{1u}$	1.774	1.752	1.712	1.405	$12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^2 11b_{1u}^2 2b_{2g}^1 9b_{3g}^0 2a_u^0$ (57%)
^3A_u	2.905	2.524	2.330	1.057	$12a_g^2 3b_{3u}^0 10b_{2u}^1 2b_{1g}^2 11b_{1u}^2 2b_{2g}^1 9b_{3g}^0 2a_u^0$ (58%)
^1A_u	2.980	2.618	2.433	1.181	$12a_g^2 3b_{3u}^0 10b_{2u}^1 2b_{1g}^2 11b_{1u}^2 2b_{2g}^1 9b_{3g}^0 2a_u^0$ (55%)
$^1B_{2u}$	3.464	3.084	2.838	2.060	$12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^1 11b_{1u}^2 2b_{2g}^2 9b_{3g}^0 2a_u^0$ (44%)
$^3B_{1g}$	3.515	3.186	3.016	2.824	$12a_g^2 3b_{3u}^0 10b_{2u}^0 2b_{1g}^2 11b_{1u}^2 2b_{2g}^1 9b_{3g}^1 2a_u^0$ (48%)
$^3B_{3u}$	3.520	3.029	2.787	1.439	$12a_g^2 3b_{3u}^0 10b_{2u}^1 2b_{1g}^1 11b_{1u}^2 2b_{2g}^2 9b_{3g}^0 2a_u^0$ (59%)
$^1B_{1g}$	3.525	3.217	3.054	1.989	$12a_g^2 3b_{3u}^0 10b_{2u}^0 2b_{1g}^2 11b_{1u}^2 2b_{2g}^1 9b_{3g}^1 2a_u^0$ (45%)
$^1B_{3u}$	3.628	3.109	2.847	1.432	$12a_g^2 3b_{3u}^0 10b_{2u}^1 2b_{1g}^1 11b_{1u}^2 2b_{2g}^2 9b_{3g}^0 2a_u^0$ (59%)
$^1B_{1u}$	4.067	3.807	3.669	2.080	$12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^2 11b_{1u}^2 2b_{2g}^1 9b_{3g}^0 2a_u^0$ (46%)
$^1B_{3g}$	4.125	4.144	4.125	5.402	$12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^2 11b_{1u}^1 2b_{2g}^1 9b_{3g}^1 2a_u^0$ (26%)
$^3B_{2g}$	4.221	3.743	3.507	2.238	$12a_g^2 3b_{3u}^0 10b_{2u}^0 2b_{1g}^1 11b_{1u}^2 2b_{2g}^2 9b_{3g}^1 2a_u^0$ (54%)
$^1B_{2g}$	4.342	3.834	3.576	2.226	$12a_g^2 3b_{3u}^0 10b_{2u}^0 2b_{1g}^1 11b_{1u}^2 2b_{2g}^2 9b_{3g}^1 2a_u^0$ (54%)
^3A_g	4.804	4.788	4.761	5.451	$12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^1 11b_{1u}^1 2b_{2g}^2 9b_{3g}^1 2a_u^0$ (23%)

[a] Closed shell part: $11a_g^2 2b_{3u}^2 9b_{2u}^2 1b_{1g}^2 10b_{1u}^2 1b_{2g}^2 8b_{3g}^2 1a_u^2$.

[b] MR-CISD configuration percentage in parentheses.

[c] Total energies (hartree): ^1A_g CASSCF/6-31G* = -535.6751476; ^1A_g MR-CISD/6-31G* = -536.9015422; ^1A_g MR-CISD + Q/6-31G* = -537.1933974; B3-LYP/6-31G* = -538.7885053.

Table 2S. Excitation energies (eV) for sixteen states of pyrene-2C calculated with CASSCF, MRCI and MRCI+Q using a CAS (8,8) reference space at the unrelaxed geometry with the 6-31G basis set.

State	CASSCF	MRCI	MRCI+Q	Config.[a,b]
^1A_g	0.000[c]	0.000[c]	0.000[c]	..12$a_g^2$3$b_{3u}^0$10$b_{2u}^0$2$b_{1g}^2$11$b_{1u}^2$2$b_{2g}^2$9$b_{3g}^0$2a_u^0 (54%)
$^3B_{3g}$	1.588	1.646	1.659	..12$a_g^2$3$b_{3u}^0$10$b_{2u}^1$2$b_{1g}^2$11$b_{1u}^1$2$b_{2g}^2$9$b_{3g}^0$2a_u^0 (42%)
$^3B_{2u}$	1.712	1.807	1.839	..12$a_g^2$3$b_{3u}^0$10$b_{2u}^0$2$b_{1g}^2$11$b_{1u}^1$2$b_{2g}^2$9$b_{3g}^1$2a_u^0 (31%)
$^3B_{1u}$	1.794	1.742	1.678	..12$a_g^2$3$b_{3u}^1$10$b_{2u}^0$2$b_{1g}^2$11$b_{1u}^2$2$b_{2g}^1$9$b_{3g}^0$2a_u^0 (58%)
^3A_u	2.966	2.592	2.408	..12$a_g^2$3$b_{3u}^0$10$b_{2u}^1$2$b_{1g}^2$11$b_{1u}^2$2$b_{2g}^1$9$b_{3g}^0$2a_u^0 (59%)
^1A_u	3.039	2.691	2.520	..12$a_g^2$3$b_{3u}^0$10$b_{2u}^1$2$b_{1g}^2$11$b_{1u}^2$2$b_{2g}^1$9$b_{3g}^0$2a_u^0 (56%)
$^1B_{2u}$	3.473	3.001	2.696	..12$a_g^2$3$b_{3u}^1$10$b_{2u}^0$2$b_{1g}^1$11$b_{1u}^2$2$b_{2g}^2$9$b_{3g}^0$2a_u^0 (43%)
$^3B_{1g}$	3.561	3.259	3.102	..12$a_g^2$3$b_{3u}^0$10$b_{2u}^0$2$b_{1g}^2$11$b_{1u}^2$2$b_{2g}^1$9$b_{3g}^1$2a_u^0 (49%)
$^3B_{3u}$	3.625	3.110	2.871	..12$a_g^2$3$b_{3u}^0$10$b_{2u}^1$2$b_{1g}^1$11$b_{1u}^2$2$b_{2g}^2$9$b_{3g}^0$2a_u^0 (60%)
$^1B_{1g}$	3.572	3.291	3.142	..12$a_g^2$3$b_{3u}^0$10$b_{2u}^0$2$b_{1g}^2$11$b_{1u}^2$2$b_{2g}^1$9$b_{3g}^1$2a_u^0 (45%)
$^1B_{3u}$	3.737	3.188	2.925	..12$a_g^2$3$b_{3u}^0$10$b_{2u}^1$2$b_{1g}^1$11$b_{1u}^2$2$b_{2g}^2$9$b_{3g}^0$2a_u^0 (60%)
$^1B_{1u}$	4.168	3.918	3.795	..12$a_g^2$3$b_{3u}^1$10$b_{2u}^0$2$b_{1g}^2$11$b_{1u}^2$2$b_{2g}^1$9$b_{3g}^0$2a_u^0 (47%)
$^1B_{3g}$	4.185	4.225	4.192	..12$a_g^2$3$b_{3u}^1$10$b_{2u}^0$2$b_{1g}^2$11$b_{1u}^1$2$b_{2g}^1$9$b_{3g}^1$2a_u^0 (26%)
$^3B_{2g}$	4.303	3.822	3.593	..12$a_g^2$3$b_{3u}^0$10$b_{2u}^0$2$b_{1g}^1$11$b_{1u}^2$2$b_{2g}^2$9$b_{3g}^1$2a_u^0 (54%)
$^1B_{2g}$	4.429	3.912	3.657	..12$a_g^2$3$b_{3u}^0$10$b_{2u}^0$2$b_{1g}^1$11$b_{1u}^2$2$b_{2g}^2$9$b_{3g}^1$2a_u^0 (55%)
^3A_g	4.888	4.907	4.896	...12$a_g^2$3$b_{3u}^1$10$b_{2u}^0$2$b_{1g}^1$11$b_{1u}^1$2$b_{2g}^2$9$b_{3g}^1$2a_u^0 (20%)

[a] Closed shell part: 11$a_g^2$2$b_{3u}^2$9$b_{2u}^2$1$b_{1g}^2$10$b_{1u}^2$1$b_{2g}^2$8$b_{3g}^2$1a_u^2.

[b] MR-CISD configuration percentage in parentheses.

[c] Total energies (hartree): ^1A_g CASSCF/6-31G = -535.4933699; ^1A_g MR-CISD/6-31G = -536.3890734; ^1A_g MR-CISD + Q/6-31G = -536.5934390.

Table 3S. Natural orbital occupation for some selected orbitals for pyrene-2C at the unrelaxed geometry calculated at MRCI (8,8)/6-31G*.

MRCI – ^1A_g	MRCI – $^3B_{3g}$	MRCI - $^3B_{1u}$
Orbital (Nat. orb. occ.)	Orbital (Nat. orb. occ.)	Orbital (Nat. orb. occ.)
$11a_g$ (1.98223039)	$11a_g$ (1.98225072)	$11a_g$ (1.98230100)
$12a_g$ (1.77548730)	$12a_g$ (1.55047913)	$12a_g$ (1.77372990)
$13a_g$ (0.00994673)	$13a_g$ (0.00994111)	$13a_g$ (0.00968966)
$2b_{3u}$ (1.97947077)	$2b_{3u}$ (1.97948033)	$2b_{3u}$ (1.97936312)
$3b_{3u}$ (0.13034127)	$3b_{3u}$ (0.15094696)	$3b_{3u}$ (0.99213563)
$4b_{3u}$ (0.01159742)	$4b_{3u}$ (0.01169473)	$4b_{3u}$ (0.01227698)
$9b_{2u}$ (1.98197754)	$9b_{2u}$ (1.98199882)	$9b_{2u}$ (1.98205227)
$10b_{2u}$ (0.26054568)	$10b_{2u}$ (0.79231361)	$10b_{2u}$ (0.26383176)
$11b_{2u}$ (0.01009639)	$11b_{2u}$ (0.01008829)	$11b_{2u}$ (0.00993043)
$1b_{1g}$ (1.98188596)	$1b_{1g}$ (1.98185141)	$1b_{1g}$ (1.98067271)
$2b_{1g}$ (1.90486568)	$2b_{1g}$ (1.90366072)	$2b_{1g}$ (1.94544653)
$3b_{1g}$ (0.01546493)	$3b_{1g}$ (0.01545098)	$3b_{1g}$ (0.01629503)
$10b_{1u}$ (1.98252852)	$10b_{1u}$ (1.98255546)	$10b_{1u}$ (1.98266724)
$11b_{1u}$ (1.72213800)	$11b_{1u}$ (1.19917848)	$11b_{1u}$ (1.71921888)
$12b_{1u}$ (0.00942145)	$12b_{1u}$ (0.00941138)	$12b_{1u}$ (0.00957787)
$1b_{2g}$ (1.98245913)	$1b_{2g}$ (1.98246173)	$1b_{2g}$ (1.98174599)
$2b_{2g}$ (1.86060782)	$2b_{2g}$ (1.83978680)	$2b_{2g}$ (0.99959562)
$3b_{2g}$ (0.01480297)	$3b_{2g}$ (0.01479446)	$3b_{2g}$ (0.01487371)
$8b_{3g}$ (1.98235891)	$8b_{3g}$ (1.98235976)	$8b_{3g}$ (1.98249202)
$9b_{3g}$ (0.23220174)	$9b_{3g}$ (0.44731725)	$9b_{3g}$ (0.23368907)
$10b_{3g}$ (0.00977092)	$10b_{3g}$ (0.00976031)	$10b_{3g}$ (0.00987048)

$1a_u$ (1.97807478)	$1a_u$ (1.97813966)	$1a_u$ (1.97729842)
$2a_u$ (0.09124009)	$2a_u$ (0.09259716)	$2a_u$ (0.04972482)
$3a_u$ (0.01162084)	$3a_u$ (0.01160721)	$3a_u$ (0.01297954)

MRCI - $^3B_{2u}$	MRCI – ^3A_u	MRCI – ^1A_u
Orbital (Nat. orb. occ.)	Orbital (Nat. orb. occ.)	Orbital (Nat. orb. occ.)
$11a_g$ (1.98224637)	$11a_g$ (1.98242448)	$11a_g$ (1.98243489)
$12a_g$ (1.40742590)	$12a_g$ (1.87717443)	$12a_g$ (1.87606183)
$13a_g$ (0.00993102)	$13a_g$ (0.00977030)	$13a_g$ (0.00973718)
$2b_{3u}$ (1.97948549)	$2b_{3u}$ (1.97906884)	$2b_{3u}$ (1.97914533)
$3b_{3u}$ (0.16034013)	$3b_{3u}$ (0.12797177)	$3b_{3u}$ (0.16461178)
$4b_{3u}$ (0.01169117)	$4b_{3u}$ (0.01092646)	$4b_{3u}$ (0.01101337)
$9b_{2u}$ (1.98199352)	$9b_{2u}$ (1.98221168)	$9b_{2u}$ (1.98221956)
$10b_{2u}$ (0.59304587)	$10b_{2u}$ (0.98975513)	$10b_{2u}$ (0.96105449)
$11b_{2u}$ (0.01009264)	$11b_{2u}$ (0.00998619)	$11b_{2u}$ (0.00998034)
$1b_{1g}$ (1.98184771)	$1b_{1g}$ (1.98029584)	$1b_{1g}$ (1.98013750)
$2b_{1g}$ (1.89811289)	$2b_{1g}$ (1.92929624)	$2b_{1g}$ (1.91918899)
$3b_{1g}$ (0.01541596)	$3b_{1g}$ (0.01403642)	$3b_{1g}$ (0.01416114)
$10b_{1u}$ (1.98256151)	$10b_{1u}$ (1.98271802)	$10b_{1u}$ (1.98273394)
$11b_{1u}$ (1.33569067)	$11b_{1u}$ (1.82394388)	$11b_{1u}$ (1.82312683)
$12b_{1u}$ (0.00941504)	$12b_{1u}$ (0.00946143)	$12b_{1u}$ (0.00946692)
$1b_{2g}$ (1.98244158)	$1b_{2g}$ (1.98180649)	$1b_{2g}$ (1.98171750)
$2b_{2g}$ (1.83189488)	$2b_{2g}$ (0.90602246)	$2b_{2g}$ (0.88100171)
$3b_{2g}$ (0.01479696)	$3b_{2g}$ (0.01342450)	$3b_{2g}$ (0.01347195)
$8b_{3g}$ (1.98236838)	$8b_{3g}$ (1.98259837)	$8b_{3g}$ (1.98261173)

$9b_{3g}$ (0.65306112)	$9b_{3g}$ (0.27586696)	$9b_{3g}$ (0.30591264)
$10b_{3g}$ (0.00977117)	$10b_{3g}$ (0.00982871)	$10b_{3g}$ (0.00983318)
$1a_u$ (1.97813288)	$1a_u$ (1.97661256)	$1a_u$ (1.97631214)
$2a_u$ (0.09661929)	$2a_u$ (0.05150289)	$2a_u$ (0.05031433)
$3a_u$ (0.01163170)	$3a_u$ (0.01129056)	$3a_u$ (0.01159956)

Table 4S. Excitation energies (eV) and optimized C_7-C_8 distance (Å)[a] for the pyrene-2C structure using a CAS (8,8) reference space with 6-31G basis set.

State	CASSCF	MRCI[b]	MRCI+Q[b]	C_7-C_8	Config.[c,d]
^1A_g	0.000[e]	0.000[e]	0.000[e]	1.540	$12a_g^2 3b_{3u}^0 10b_{2u}^0 2b_{1g}^2 11b_{1u}^2 2b_{2g}^2 9b_{3g}^0 2a_u^0$ (69%)
$^3B_{2u}$	1.197	1.138	1.097	1.474	$..12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^1 11b_{1u}^2 2b_{2g}^2 9b_{3g}^0 2a_u^0$ (75%)
$^3B_{1u}$	1.637	1.652	1.620	1.527	$12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^2 11b_{1u}^2 2b_{2g}^1 9b_{3g}^0 2a_u^0$ (75%)
$^1B_{2u}$	1.884	1.463	1.215	1.470	$12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^1 11b_{1u}^2 2b_{2g}^2 9b_{3g}^0 2a_u^0$ (73%)

[a] C_7-C_8 distance = C_9-C_{10} distance
[b] Single point calculation at CASCSF (8,8) optimized geometries.
[c] Closed shell part: $11a_g^2 2b_{3u}^2 9b_{2u}^2 1b_{1g}^2 10b_{1u}^2 1b_{2g}^2 8b_{3g}^2 1a_u^2$.
[d] MRCI configuration percentage in parentheses.
[e] Total energies (hartree): ^1A_g CASSCF/6-31G = -535.7194348; ^1A_g MRCI/6-31G = -536.6165891; ^1A_g MRSD + Q/6-31G = -537.1542770.

Table 5S. Natural orbital occupation for some selected orbitals for pyrene-2C at the relaxed geometry calculated at MRCI (8,8)/6-31G*.

MRCI – ^1A_g	MRCI – $^3B_{2u}$	MRCI - $^1B_{2u}$	MRCI - $^3B_{1u}$
Orbital (Nat. orb. occ.)	Orbital (Nat. orb. occ.)	Orbital (Nat. orb. occ.)	Orbital (Nat. orb. occ.)
$11a_g$ (1.98244690)	$11a_g$ (1.98245433)	$11a_g$ (1.98259581)	$11a_g$ (1.98255383)
$12a_g$ (1.97115409)	$12a_g$ (1.97343336)	$12a_g$ (1.97381176)	$12a_g$ (1.97171347)
$13a_g$ (0.00969937)	$13a_g$ (0.00993824)	$13a_g$ (0.00988698)	$13a_g$ (0.01017639)
$2b_{3u}$ (1.97948847)	$2b_{3u}$ (1.98019266)	$2b_{3u}$ (1.97978520)	$2b_{3u}$ (1.97941426)
$3b_{3u}$ (0.11400285)	$3b_{3u}$ (0.99560639)	$3b_{3u}$ (1.00876630)	$3b_{3u}$ (0.99513072)
$4b_{3u}$ (0.01222407)	$4b_{3u}$ (0.01228313)	$4b_{3u}$ (0.01270746)	$4b_{3u}$ (0.01302365)
$9b_{2u}$ (1.98167425)	$9b_{2u}$ (1.98151527)	$9b_{2u}$ (1.98163463)	$9b_{2u}$ (1.98173715)
$10b_{2u}$ (0.02195904)	$10b_{2u}$ (0.01973926)	$10b_{2u}$ (0.01930241)	$10b_{2u}$ (0.02169009)
$11b_{2u}$ (0.00962568)	$11b_{2u}$ (0.00972347)	$11b_{2u}$ (0.00966503)	$11b_{2u}$ (0.00984887)
$1b_{1g}$ (1.98118337)	$1b_{1g}$ (1.98095129)	$1b_{1g}$ (1.98099602)	$1b_{1g}$ (1.98066718)
$2b_{1g}$ (1.89572920)	$2b_{1g}$ (0.99774654)	$2b_{1g}$ (0.98617754)	$2b_{1g}$ (1.97105340)
$3b_{1g}$ (0.01368875)	$3b_{1g}$ (0.01367521)	$3b_{1g}$ (0.01376918)	$3b_{1g}$ (0.01380125)
$10b_{1u}$ (1.98336562)	$10b_{1u}$ (1.98331911)	$10b_{1u}$ (1.98345427)	$10b_{1u}$ (1.98327069)
$11b_{1u}$ (1.97089137)	$11b_{1u}$ (1.97311425)	$11b_{1u}$ (1.97348141)	$11b_{1u}$ (1.97139417)
$12b_{1u}$ (0.00990746)	$12b_{1u}$ (0.01001421)	$12b_{1u}$ (0.00994954)	$12b_{1u}$ (0.00973438)
$1b_{2g}$ (1.98293906)	$1b_{2g}$ (1.98228624)	$1b_{2g}$ (1.98241830)	$1b_{2g}$ (1.98203248)
$2b_{2g}$ (1.88771349)	$2b_{2g}$ (1.97315830)	$2b_{2g}$ (1.94324429)	$2b_{2g}$ (0.99671738)
$3b_{2g}$ (0.01433113)	$3b_{2g}$ (0.01378290)	$3b_{2g}$ (0.01481650)	$3b_{2g}$ (0.01456207)
$8b_{3g}$ (1.98253637)	$8b_{3g}$ (1.98232673)	$8b_{3g}$ (1.98244518)	$8b_{3g}$ (1.98241765)
$9b_{3g}$ (0.02205049)	$9b_{3g}$ (0.01978077)	$9b_{3g}$ (0.01940281)	$9b_{3g}$ (0.02161946)

$10b_{3g}$ (0.00989123)	$10b_{3g}$ (0.00992410)	$10b_{3g}$ (0.00984799)	$10b_{3g}$ (0.00980780)
$1a_u$ (1.97831651)	$1a_u$ (1.97617198)	$1a_u$ (1.97435308)	$1a_u$ (1.97833598)
$2a_u$ (0.09137147)	$2a_u$ (0.02136074)	$2a_u$ (0.05235988)	$2a_u$ (0.02377575)
$3a_u$ (0.01025735)	$3a_u$ (0.01219772)	$3a_u$ (0.01040753)	$3a_u$ (0.01230762)

Table 6S. Occupation schemes for the DFT calculations.

	^1A_g	$^3B_{3g}$	$^3B_{2u}$	$^3B_{1u}$	^3A_u	^1A_u	$^1B_{2u}$	$^3B_{1g}$
alpha								
a_g	1-12	1-12	1-12	1-12	1-12	1-12	1-12	1-12
b_{3u}	1-2	1-2	1-2	1-3	1-2	1-2	1-3	1-2
b_{2u}	1-9	1-10	1-9	1-9	1-10	1-10	1-9	1-9
b_{1g}	1-2	1-2	1-2	1-2	1-2	1-2	1	1-2
b_{1u}	1-11	1-11	1-11	1-11	1-11	1-11	1-11	1-11
b_{2g}	1-2	1-2	1-2	1-2	1-2	1	1-2	1-2
b_{3g}	1-8	1-8	1-9	1-8	1-8	1-8	1-8	1-9
a_u	1	1	1	1	1	1	1	1
beta								
a_g	1-12	1-12	1-12	1-12	1-12	1-12	1-12	1-12
b_{3u}	1-2	1-2	1-2	1-2	1-2	1-2	1-2	1-2
b_{2u}	1-9	1-9	1-9	1-9	1-9	1-9	1-9	1-9
b_{1g}	1-2	1-2	1-2	1-2	1-2	1-2	1-2	1-2
b_{1u}	1-11	1-10	1-10	1-11	1-11	1-11	1-11	1-11
b_{2g}	1-2	1-2	1-2	1	1	1-2	1-2	1
b_{3g}	1-8	1-8	1-8	1-8	1-8	1-8	1-8	1-8
a_u	1	1	1	1	1	1	1	1
	$^3B_{3u}$	$^1B_{1g}$	$^1B_{3u}$	$^1B_{1u}$	$^1B_{3g}$	$^3B_{2g}$	$^1B_{2g}$	^3A_g

alpha								
a_g	1-12	1-12	1-12	1-12	1-12	1-12	1-12	1-12
b_{1g}	1-2	1-2	1-2	1-3	1-3	1-2	1-2	1-3
b_{2g}	1-10	1-9	1-10	1-9	1-9	1-9	1-9	1-9
b_{3g}	1-2	1-2	1	1-2	1-2	1-2	1-2	1-2
a_u	1-11	1-11	1-11	1-11	1-11	1-11	1-11	1-11
b_{1u}	1-2	1-2	1-2	1	1	1-2	1-2	1-2
b_{2u}	1-8	1-8	1-8	1-8	1-8	1-9	1-8	1-9
b_{3u}	1	1	1	1	1	1	1	1
beta								
a_g								
b_{1g}	1-12	1-12	1-12	1-12	1-12	1-12	1-12	1-12
b_{2g}	1-2	1-2	1-2	1-2	1-2	1-2	1-2	1-2
b_{3g}	1-9	1-9	1-9	1-9	1-9	1-9	1-9	1-9
a_u	1	1-2	1-2	1-2	1-2	1	1	1
b_{1u}	1-11	1-11	1-11	1-11	1-10	1-11	1-11	1-11
b_{2u}	1-2	1	1-2	1-2	1-2	1-2	1-2	1-2
b_{3u}	1-8	1-9	1-8	1-8	1-9	1-8	1-9	1-8
	1	1	1	1	1	1	1	1

Table 7S. Excitation energies (eV) for the unrelaxed pyrene-2C structure using B3-LYP, PBE and PBE0, together with the 6-31G* basis set.

State	B3-LYP	PBE	PBE0	Configuration[a]
^1A_g	0.000[b]	0.000[b]	0.000[b]	$..12a_g^2 3b_{3u}^0 10b_{2u}^0 2b_{1g}^2 11b_{1u}^2 2b_{2g}^2 9b_{3g}^0 2a_u^0$
$^3B_{3g}$	1.616	1.620	1.634	$...12a_g^2 3b_{3u}^0 10b_{2u}^1 2b_{1g}^2 11b_{1u}^1 2b_{2g}^2 9b_{3g}^0 2a_u^0$
$^3B_{2u}$	1.927	1.918	1.930	$.. 12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^1 11b_{1u}^2 2b_{2g}^2 9b_{3g}^0 2a_u^0$
$^3B_{1u}$	1.405	1.553	1.328	$...12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^2 11b_{1u}^2 2b_{2g}^1 9b_{3g}^0 2a_u^0$
^3A_u	1.057	1.210	1.099	$...12a_g^2 3b_{3u}^0 10b_{2u}^1 2b_{1g}^2 11b_{1u}^2 2b_{2g}^1 9b_{3g}^0 2a_u^0$
^1A_u	1.181	1.314	1.238	$...12a_g^2 3b_{3u}^0 10b_{2u}^1 2b_{1g}^2 11b_{1u}^2 2b_{2g}^1 9b_{3g}^0 2a_u^0$
$^1B_{2u}$	2.060	1.983	2.072	$..12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^1 11b_{1u}^2 2b_{2g}^2 9b_{3g}^0 2a_u^0$
$^3B_{1g}$	1.855	1.965	1.919	$..12a_g^2 3b_{3u}^0 10b_{2u}^0 2b_{1g}^2 11b_{1u}^2 2b_{2g}^1 9b_{3g}^1 2a_u^0$
$^3B_{3u}$	1.439	1.493	1.516	$...12a_g^2 3b_{3u}^0 10b_{2u}^1 2b_{1g}^1 11b_{1u}^2 2b_{2g}^2 9b_{3g}^0 2a_u^0$
$^1B_{1g}$	1.989	2.075	2.069	$..12a_g^2 3b_{3u}^0 10b_{2u}^0 2b_{1g}^2 11b_{1u}^2 2b_{2g}^1 9b_{3g}^1 2a_u^0$
$^1B_{3u}$	1.432	1.498	1.500	$...12a_g^2 3b_{3u}^0 10b_{2u}^1 2b_{1g}^1 11b_{1u}^2 2b_{2g}^2 9b_{3g}^0 2a_u^0$
$^1B_{1u}$	2.080	1.919	2.133	$...12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^2 11b_{1u}^2 2b_{2g}^1 9b_{3g}^0 2a_u^0$
$^1B_{3g}$	2.407	2.183	2.495	$...12a_g^2 3b_{3u}^0 10b_{2u}^1 2b_{1g}^2 11b_{1u}^1 2b_{2g}^2 9b_{3g}^0 2a_u^0$
$^3B_{2g}$	2.238	2.248	2.337	$...12a_g^2 3b_{3u}^0 10b_{2u}^0 2b_{1g}^1 11b_{1u}^2 2b_{2g}^2 9b_{3g}^1 2a_u^0$
$^1B_{2g}$	2.226	2.251	2.316	$...12a_g^2 3b_{3u}^0 10b_{2u}^0 2b_{1g}^1 11b_{1u}^2 2b_{2g}^2 9b_{3g}^1 2a_u^0$
^3A_g	5.451	4.976	5.604	$...12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^1 11b_{1u}^1 2b_{2g}^2 9b_{3g}^1 2a_u^0$

[a] Closed shell part: $11a_g^2 2b_{3u}^2 9b_{2u}^2 1b_{1g}^2 10b_{1u}^2 1b_{2g}^2 8b_{3g}^2 1a_u^2$.
[b] Total energies (hartree): 1Ag B3-LYP = -538.7885053; PBE = -538.4651999; PBE0 = -538.4763159.

Table 8S: Excitation energies ΔE (eV) and optimized C_7-C_8 distance (Å)[a] for the relaxed pyrene-2C structure using B3-LYP, PBE and PBE0 with the 6-31G* basis set.

State	B3-LYP		PBE		PBE0		Config.[b]
	ΔE	C_7-C_8	ΔE	C_7-C_8	ΔE	C_7-C_8	
^1A_g	0.000[c]	1.515	0.000[c]	1.515	0.000[c]	1.506	$12a_g^2 3b_{3u}^0 10b_{2u}^0 2b_{1g}^2 11b_{1u}^2 2b_{2g}^2 9b_{3g}^0 2a_u^0$
$^3B_{2u}$	0.441	1.454	0.493	1.459	0.384	1.448	$12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^1 11b_{1u}^2 2b_{2g}^2 9b_{3g}^0 2a_u^0$
$^1B_{2u}$	0.479	1.453	0.525	1.458	0.417	1.446	$12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^1 11b_{1u}^2 2b_{2g}^2 9b_{3g}^0 2a_u^0$
$^3B_{1u}$	1.430	1.502	1.570	1.504	1.353	1.494	$12a_g^2 3b_{3u}^1 10b_{2u}^0 2b_{1g}^2 11b_{1u}^2 2b_{2g}^1 9b_{3g}^0 2a_u^0$

[a] C_7-C_8 and C_9-C_{10} distances are symmetry equivalent.
[b] Closed shell part: $11a_g^2 2b_{3u}^2 9b_{2u}^2 1b_{1g}^2 10b_{1u}^2 1b_{2g}^2 8b_{3g}^2 1a_u^2$.
[c] ^1A_g B3-LYP = -539.05378069; PBE = -538.7157240; PBE0 = -538.7620796.

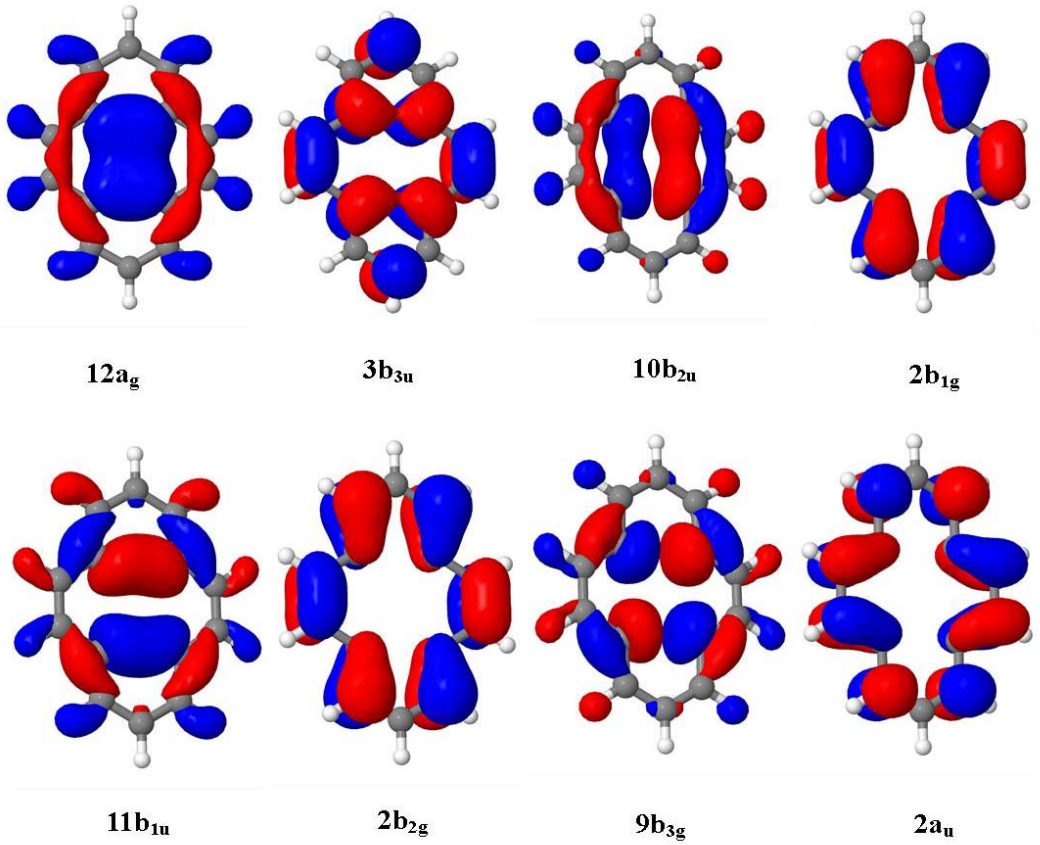

Figure 1S. Molecular orbitals for the ^1A_g state computed at the B3-LYP/6-31G* level for the unrelaxed structure.

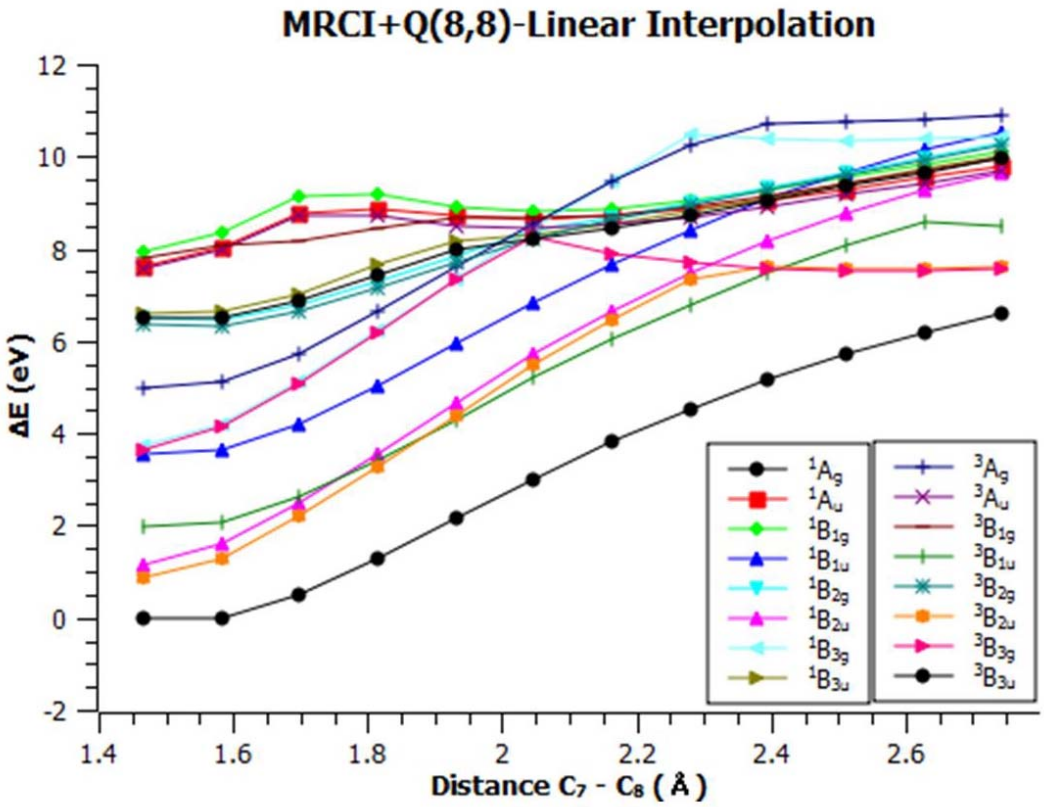

Figure 2S. Linear Interpolation for sixteen states of pyrene-2C computed at MRCI + Q (8,8)/6-31G* level. Paths between the structures with C_7-C_8 and C_9-C_{10} = 1.467 to 2.744 Å; energies are relative to E(^1A_g) = -537.4386964 hartree.

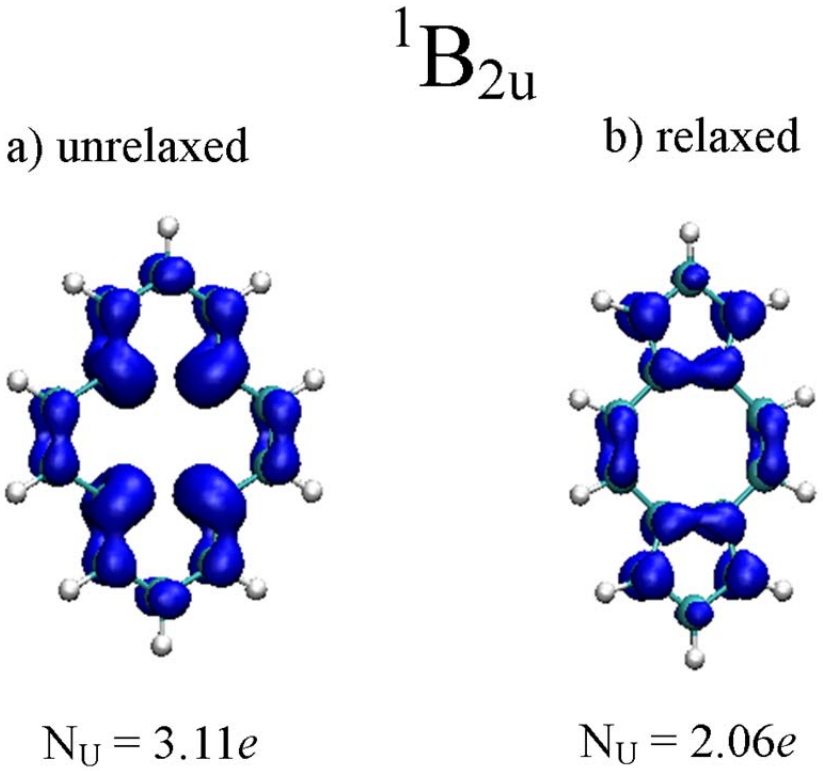

Figure 3S. Unpaired electron density plots for the $^1B_{2u}$ state using the MR-CISD/6-31G* approach. a), unrelaxed geometry, b), relaxed geometry. Isodensity value is 0.007 *e*/bohr^3.

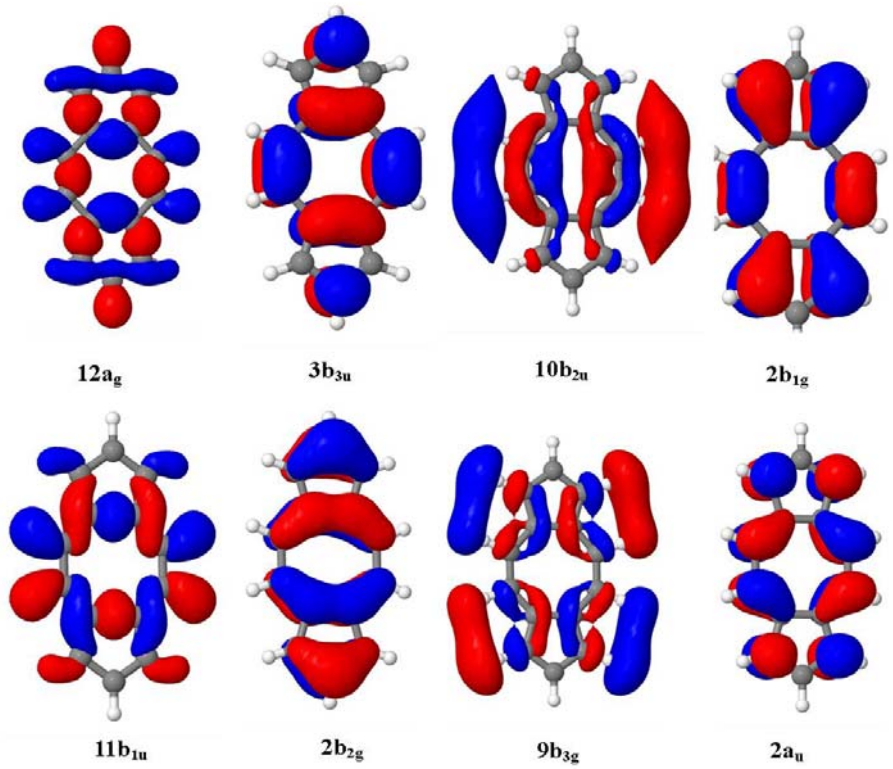

Figure 4S. Active molecular orbitals for the ^1A_g state computed at the B3-LYP/6-31G* level for the relaxed structure.

Cartesian geometries (Å)

Pyrene

Geometry optimization at DFT/B3-LYP_Gaussian/6-31G** level

C	0.000000	0.000000	3.523415
C	0.000000	0.000000	-3.523415
C	0.000000	1.210522	2.832749
C	0.000000	1.210522	-2.832749
C	0.000000	-1.210522	2.832749
C	0.000000	-1.210522	-2.832749
C	0.000000	1.236204	1.428935
C	0.000000	1.236204	-1.428935
C	0.000000	-1.236204	1.428935
C	0.000000	-1.236204	-1.428935
C	0.000000	0.000000	0.713276
C	0.000000	0.000000	-0.713276
C	0.000000	2.463838	0.680667
C	0.000000	2.463838	-0.680667
C	0.000000	-2.463838	-0.680667
C	0.000000	-2.463838	0.680667
H	0.000000	2.149861	-3.379217
H	0.000000	-3.401692	1.229891
H	0.000000	-3.401692	-1.229891
H	0.000000	3.401692	1.229891
H	0.000000	0.000000	4.609494
H	0.000000	2.149861	3.379217
H	0.000000	-2.149861	3.379217
H	0.000000	3.401692	-1.229891
H	0.000000	0.000000	-4.609494
H	0.000000	-2.149861	-3.379217

Pyrene-2C-relaxed

Geometry optimization at CASSCF(8,8)/6-31G* level

^1A_g

C	0.000000	0.000000	3.842357
C	0.000000	0.000000	-3.842357
C	0.000000	1.138177	3.044674
C	0.000000	-1.138177	3.044674
C	0.000000	1.138177	-3.044674
C	0.000000	-1.138177	-3.044674
C	0.000000	0.767298	1.698493
C	0.000000	-0.767298	1.698493
C	0.000000	0.767298	-1.698493
C	0.000000	-0.767298	-1.698493
C	0.000000	1.724327	0.693931
C	0.000000	-1.724327	0.693931
C	0.000000	1.724327	-0.693931
C	0.000000	-1.724327	-0.693931
H	0.000000	2.152054	3.393591
H	0.000000	-2.152054	3.393591
H	0.000000	2.152054	-3.393591
H	0.000000	-2.152054	-3.393591
H	0.000000	2.722714	1.097789
H	0.000000	-2.722714	1.097789
H	0.000000	2.722714	-1.097789
H	0.000000	-2.722714	-1.097789
H	0.000000	0.000000	4.916072
H	0.000000	0.000000	-4.916072

$^3B_{2u}$

C	0.000000	0.000000	3.862187
C	0.000000	0.000000	-3.862187
C	0.000000	1.116529	3.039605
C	0.000000	-1.116529	3.039605
C	0.000000	1.116529	-3.039605
C	0.000000	-1.116529	-3.039605
C	0.000000	0.735975	1.672155
C	0.000000	-0.735975	1.672155
C	0.000000	0.735975	-1.672155
C	0.000000	-0.735975	-1.672155
C	0.000000	1.734203	0.691061
C	0.000000	-1.734203	0.691061
C	0.000000	1.734203	-0.691061
C	0.000000	-1.734203	-0.691061
H	0.000000	2.137470	3.372057
H	0.000000	-2.137470	3.372057
H	0.000000	2.137470	-3.372057
H	0.000000	-2.137470	-3.372057
H	0.000000	2.726052	1.110185
H	0.000000	-2.726052	1.110185
H	0.000000	2.726052	-1.110185
H	0.000000	-2.726052	-1.110185
H	0.000000	0.000000	4.933710
H	0.000000	0.000000	-4.933710

$^3B_{1u}$

C	0.000000	0.000000	3.855285
C	0.000000	0.000000	-3.855285
C	0.000000	1.148351	3.023772
C	0.000000	-1.148351	3.023772
C	0.000000	1.148351	-3.023772
C	0.000000	-1.148351	-3.023772
C	0.000000	0.760240	1.716697
C	0.000000	-0.760240	1.716697
C	0.000000	0.760240	-1.716697
C	0.000000	-0.760240	-1.716697
C	0.000000	1.771413	0.666093
C	0.000000	-1.771413	0.666093
C	0.000000	1.771413	-0.666093
C	0.000000	-1.771413	-0.666093
H	0.000000	2.163600	3.368337
H	0.000000	-2.163600	3.368337
H	0.000000	2.163600	-3.368337
H	0.000000	-2.163600	-3.368337
H	0.000000	2.758953	1.095374
H	0.000000	-2.758953	1.095374
H	0.000000	2.758953	-1.095374
H	0.000000	-2.758953	-1.095374
H	0.000000	0.000000	4.927761
H	0.000000	0.000000	-4.927761

$^1B_{2u}$

C	0.000000	0.000000	3.865724
C	0.000000	0.000000	-3.865724
C	0.000000	1.118101	3.045050
C	0.000000	-1.118101	3.045050
C	0.000000	1.118101	-3.045050
C	0.000000	-1.118101	-3.045050
C	0.000000	0.733372	1.671204
C	0.000000	-0.733372	1.671204
C	0.000000	0.733372	-1.671204
C	0.000000	-0.733372	-1.671204
C	0.000000	1.729144	0.688085
C	0.000000	-1.729144	0.688085
C	0.000000	1.729144	-0.688085
C	0.000000	-1.729144	-0.688085
H	0.000000	2.139334	3.374685
H	0.000000	-2.139334	3.374685
H	0.000000	2.139334	-3.374685
H	0.000000	-2.139334	-3.374685
H	0.000000	2.720855	1.107745
H	0.000000	-2.720855	1.107745
H	0.000000	2.720855	-1.107745
H	0.000000	-2.720855	-1.107745
H	0.000000	0.000000	4.937475
H	0.000000	0.000000	-4.937475

Geometry optimization at CASSCF(8,8)/6-31G level

^1A_g

C	0.000000	0.000000	3.851719
C	0.000000	0.000000	-3.851719
C	0.000000	1.139079	3.050673
C	0.000000	-1.139079	3.050673
C	0.000000	1.139079	-3.050673
C	0.000000	-1.139079	-3.050673
C	0.000000	0.769903	1.698610
C	0.000000	-0.769903	1.698610
C	0.000000	0.769903	-1.698610
C	0.000000	-0.769903	-1.698610
C	0.000000	1.726772	0.694097
C	0.000000	-1.726772	0.694097
C	0.000000	1.726772	-0.694097
C	0.000000	-1.726772	-0.694097
H	0.000000	2.150517	3.398431
H	0.000000	-2.150517	3.398431
H	0.000000	2.150517	-3.398431
H	0.000000	-2.150517	-3.398431
H	0.000000	2.724369	1.097732
H	0.000000	-2.724369	1.097732
H	0.000000	2.724369	-1.097732
H	0.000000	-2.724369	-1.097732
H	0.000000	0.000000	4.922214
H	0.000000	0.000000	-4.922214

$^3B_{2u}$

C	0.000000	0.000000	3.869223
C	0.000000	0.000000	-3.869223
C	0.000000	1.120420	3.046832
C	0.000000	-1.120420	3.046832
C	0.000000	1.120420	-3.046832
C	0.000000	-1.120420	-3.046832
C	0.000000	0.737017	1.674628
C	0.000000	-0.737017	1.674628
C	0.000000	0.737017	-1.674628
C	0.000000	-0.737017	-1.674628
C	0.000000	1.733286	0.691050
C	0.000000	-1.733286	0.691050
C	0.000000	1.733286	-0.691050
C	0.000000	-1.733286	-0.691050
H	0.000000	2.138977	3.378254
H	0.000000	-2.138977	3.378254
H	0.000000	2.138977	-3.378254
H	0.000000	-2.138977	-3.378254
H	0.000000	2.724489	1.110197
H	0.000000	-2.724489	1.110197
H	0.000000	2.724489	-1.110197
H	0.000000	-2.724489	-1.110197
H	0.000000	0.000000	4.937649
H	0.000000	0.000000	-4.937649

$^3B_{1u}$

C	0.000000	0.000000	3.862978
C	0.000000	0.000000	-3.862978
C	0.000000	1.149167	3.029419
C	0.000000	-1.149167	3.029419
C	0.000000	1.149167	-3.029419
C	0.000000	-1.149167	-3.029419
C	0.000000	0.763461	1.714790
C	0.000000	-0.763461	1.714790
C	0.000000	0.763461	-1.714790
C	0.000000	-0.763461	-1.714790
C	0.000000	1.772597	0.667994
C	0.000000	-1.772597	0.667994
C	0.000000	1.772597	-0.667994
C	0.000000	-1.772597	-0.667994
H	0.000000	2.161596	3.373426
H	0.000000	-2.161596	3.373426
H	0.000000	2.161596	-3.373426
H	0.000000	-2.161596	-3.373426
H	0.000000	2.758546	1.098543
H	0.000000	-2.758546	1.098543
H	0.000000	2.758546	-1.098543
H	0.000000	-2.758546	-1.098543
H	0.000000	0.000000	4.932825
H	0.000000	0.000000	-4.932825

$^1B_{2u}$

C	0.000000	0.000000	3.872540
C	0.000000	0.000000	-3.872540
C	0.000000	1.122050	3.051970
C	0.000000	-1.122050	3.051970
C	0.000000	1.122050	-3.051970
C	0.000000	-1.122050	-3.051970
C	0.000000	0.735019	1.673670
C	0.000000	-0.735019	1.673670
C	0.000000	0.735019	-1.673670
C	0.000000	-0.735019	-1.673670
C	0.000000	1.728557	0.688142
C	0.000000	-1.728557	0.688142
C	0.000000	1.728557	-0.688142
C	0.000000	-1.728557	-0.688142
H	0.000000	2.140726	3.381279
H	0.000000	-2.140726	3.381279
H	0.000000	2.140726	-3.381279
H	0.000000	-2.140726	-3.381279
H	0.000000	2.719760	1.106969
H	0.000000	-2.719760	1.106969
H	0.000000	2.719760	-1.106969
H	0.000000	-2.719760	-1.106969
H	0.000000	0.000000	4.941077
H	0.000000	0.000000	-4.941077

Geometry optimization at B3-3LYP/6-31G* level

^1A_g

C	0.0000000	3.8806424	0.0000000
C	0.0000000	-3.8806424	0.0000000
C	1.1445885	3.0707191	0.0000000
C	1.1445885	-3.0707191	-0.0000000
C	-1.1445885	3.0707191	0.0000000
C	-1.1445885	-3.0707191	0.0000000
C	0.7572666	1.7149436	0.0000000
C	0.7572666	-1.7149436	0.0000000
C	-0.7572666	1.7149436	0.0000000
C	-0.7572666	-1.7149436	0.0000000
C	1.7141647	0.7005301	-0.0000000
C	1.7141647	-0.7005301	0.0000000
C	-1.7141647	-0.7005301	0.0000000
C	-1.7141647	0.7005301	0.0000000
H	2.1728094	-3.4130571	0.0000000
H	-2.7265930	1.1054116	0.0000000
H	-2.7265930	-1.1054116	-0.0000000
H	2.7265930	1.1054116	0.0000000
H	0.0000000	4.9657675	0.0000000
H	2.1728094	3.4130571	0.0000000
H	-2.1728094	3.4130571	0.0000000
H	2.7265930	-1.1054116	0.0000000
H	0.0000000	-4.9657675	0.0000000
H	-2.1728094	-3.4130571	-0.0000000

$^3B_{2u}$

C	-0.0000000	3.9033487	0.0000000
C	-0.0000000	-3.9033487	0.0000000
C	1.1253816	3.0720677	-0.0000000
C	1.1253816	-3.0720677	0.0000000
C	-1.1253816	3.0720677	-0.0000000
C	-1.1253816	-3.0720677	0.0000000
C	0.7272061	1.6941606	0.0000000
C	0.7272061	-1.6941606	-0.0000000
C	-0.7272061	1.6941606	0.0000000
C	-0.7272061	-1.6941606	0.0000000
C	1.7234258	0.6951769	0.0000000
C	1.7234258	-0.6951769	0.0000000
C	-1.7234258	-0.6951769	0.0000000
C	-1.7234258	0.6951769	0.0000000
H	2.1607251	-3.3975440	0.0000000
H	-2.7287790	1.1161024	0.0000000
H	-2.7287790	-1.1161024	0.0000000
H	2.7287790	1.1161024	0.0000000
H	0.0000000	4.9863933	-0.0000000
H	2.1607251	3.3975440	0.0000000
H	-2.1607251	3.3975440	0.0000000
H	2.7287790	-1.1161024	-0.0000000
H	0.0000000	-4.9863933	-0.0000000
H	-2.1607251	-3.3975440	-0.0000000

$^3B_{1u}$

C	0.0000000	3.8862799	-0.0000000
C	0.0000000	-3.8862799	-0.0000000
C	1.1514499	3.0525606	0.0000000
C	1.1514499	-3.0525606	0.0000000
C	-1.1514499	3.0525606	0.0000000
C	-1.1514499	-3.0525606	0.0000000
C	0.7512270	1.7201799	0.0000000
C	0.7512270	-1.7201799	0.0000000
C	-0.7512270	1.7201799	-0.0000000
C	-0.7512270	-1.7201799	-0.0000000
C	1.7531609	0.6802842	0.0000000
C	1.7531609	-0.6802842	0.0000000
C	-1.7531609	-0.6802842	0.0000000
C	-1.7531609	0.6802842	-0.0000000
H	2.1806727	-3.3914315	0.0000000
H	-2.7554013	1.1082395	0.0000000
H	-2.7554013	-1.1082395	-0.0000000
H	2.7554013	1.1082395	0.0000000
H	0.0000000	4.9707360	0.0000000
H	2.1806727	3.3914315	-0.0000000
H	-2.1806727	3.3914315	0.0000000
H	2.7554013	-1.1082395	-0.0000000
H	0.0000000	-4.9707360	0.0000000
H	-2.1806727	-3.3914315	0.0000000

$^1B_{2u}$

C	0.0000000	3.9072825	0.0000000
C	0.0000000	-3.9072825	0.0000000
C	1.1265716	3.0749468	0.0000000
C	1.1265716	-3.0749468	0.0000000
C	-1.1265716	3.0749468	-0.0000000
C	-1.1265716	-3.0749468	0.0000000
C	0.7262653	1.6946500	-0.0000000
C	0.7262653	-1.6946500	0.0000000
C	-0.7262653	1.6946500	0.0000000
C	-0.7262653	-1.6946500	-0.0000000
C	1.7212139	0.6944152	0.0000000
C	1.7212139	-0.6944152	-0.0000000
C	-1.7212139	-0.6944152	-0.0000000
C	-1.7212139	0.6944152	-0.0000000
H	2.1621310	-3.3992554	0.0000000
H	-2.7267128	1.1149602	0.0000000
H	-2.7267128	-1.1149602	0.0000000
H	2.7267128	1.1149602	0.0000000
H	0.0000000	4.9903494	0.0000000
H	2.1621310	3.3992554	0.0000000
H	-2.1621310	3.3992554	0.0000000
H	2.7267128	-1.1149602	0.0000000
H	0.0000000	-4.9903494	0.0000000
H	-2.1621310	-3.3992554	0.0000000