Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Steric and Electric Field Driven Distortions in Aromatic Molecules: Spontaneous and Non-Spontaneous Symmetry Breaking

Kalishankar Bhattacharyya[1], Ammu Surendran[2], Chandra Chowdhury[1] and Ayan Datta[1*]

[1]Department of Spectroscopy, Indian Association for the Cultivation of Science, 2A and 2B Raja S.C. Mullick Road, Jadavpur-700032, Kolkata, West Bengal, India.

[2]Department of Chemistry, Cochin University of Science and Technology (CUSAT), Cochin - 682022, Kerala, India.

Contents

---

1. Cartesian coordinates for optimized structures of (a) TBP (**1**), (b) Benzene (**2**) and (c) Coronene (**3**) and their energies in Hartree and low frequencies calculated at B3LYP/6-31+G(d,p) level of theory.

(a) Tribenzopyrene (TBP, 1)

Atom	X	Y	Z
C	0.00000000	2.76756200	-2.26019010
C	0.00000000	1.39795800	-2.18192210
C	0.00000000	0.67125200	-3.42478810
H	0.00000000	1.24240900	-4.34860510

C	0.00000000	-0.67125200	-3.42478810
H	0.00000000	-1.24240900	-4.34860510
C	0.00000000	-1.39795800	-2.18192210
C	0.00000000	-2.76756200	-2.26019010
C	0.00000000	-3.57922400	-1.11712510
C	0.00000000	-4.98791900	-1.32439010
H	0.00000000	-5.34458100	-2.35091010
C	0.00000000	-5.87116400	-0.27560510
H	0.00000000	-6.94444000	-0.43859610
C	0.00000000	-5.33197200	1.02341390
H	0.00000000	-5.99204400	1.88612190
C	0.00000000	-3.96630900	1.24230790
H	0.00000000	-3.71396300	2.28139390
C	0.00000000	-2.98390900	0.19711690
C	0.00000000	-1.50409800	0.30525790
C	0.00000000	-0.72413100	1.55729490
C	0.00000000	-1.35228100	2.83073090
H	0.00000000	-2.41340700	2.89959790
C	0.00000000	-0.69567500	4.04405690
H	0.00000000	-1.26724400	4.96738090
C	-0.00000000	0.69567500	4.04405690
H	-0.00000000	1.26724400	4.96738090
C	-0.00000000	1.35228100	2.83073090
H	-0.00000000	2.41340700	2.89959790
C	-0.00000000	0.72413100	1.55729490
C	-0.00000000	1.50409800	0.30525790

C	-0.00000000	2.98390900	0.19711690
C	-0.00000000	3.96630900	1.24230790
H	-0.00000000	3.71396300	2.28139390
C	-0.00000000	5.33197200	1.02341390
H	-0.00000000	5.99204400	1.88612190
C	-0.00000000	5.87116400	-0.27560510
H	-0.00000000	6.94444000	-0.43859610
C	-0.00000000	4.98791900	-1.32439010
H	-0.00000000	5.34458100	-2.35091010
C	-0.00000000	3.57922400	-1.11712510
C	0.00000000	-0.73149000	-0.89252110
C	-0.00000000	0.73149000	-0.89252110
H	0.00000000	-3.24146800	-3.23820910
H	-0.00000000	3.24146800	-3.23820910

Energy = -1225.9649232 Hartree

Low Frequencies (cm^{-1}) : -267.392 -238.248 -31.366 26.700 99.229 120.027

(b) Benzene (2)

Atom	X	Y	Z
C	0.000000	1.396223	0.000000
C	-1.209113	0.698096	0.000000
C	-1.209113	-0.698096	0.000000
C	0.000000	-1.396223	0.000000
C	1.209113	-0.698096	0.000000

C	1.209113	0.698096	0.000000
H	0.000000	2.482284	0.000000
H	-2.149668	1.241129	0.000000
H	-2.149668	-1.241129	0.000000
H	0.000000	-2.482284	0.000000
H	2.149668	-1.241129	0.000000
H	2.149668	1.241129	0.000000

Energy = -232.2582139 Hartree

Low Frequencies (cm^{-1}) : 413.990 413.990 621.137 621.137 692.201 718.115

(c) Coronene (3)

Atom	X	Y	Z
C	1.248268	3.534175	0.000000
C	0.000000	2.848853	0.000000
C	0.000000	1.427452	0.000000
C	1.236210	0.713726	0.000000
C	2.467179	1.424426	0.000000
C	2.436551	2.848120	0.000000
C	-1.236210	0.713726	0.000000
C	1.236210	-0.713726	0.000000
C	0.000000	-1.427452	0.000000
C	-1.236210	-0.713726	0.000000
C	0.000000	-2.848853	0.000000
C	1.248268	-3.534175	0.000000

C	2.436551	-2.848120	0.000000
C	2.467179	-1.424426	0.000000
C	3.684820	-0.686056	0.000000
C	3.684820	0.686056	0.000000
H	4.624605	1.231865	0.000000
H	4.624605	-1.231865	0.000000
H	1.245477	4.620958	0.000000
H	3.379129	3.389093	0.000000
H	1.245477	-4.620958	0.000000
H	3.379129	-3.389093	0.000000
C	-1.248268	3.534175	0.000000
C	-2.436551	2.848120	0.000000
C	-2.467179	1.424426	0.000000
H	-1.245477	4.620958	0.000000
H	-3.379129	3.389093	0.000000
C	-3.684820	0.686056	0.000000
C	-3.684820	-0.686056	0.000000
C	-2.467179	-1.424426	0.000000
H	-4.624605	1.231865	0.000000
H	-4.624605	-1.231865	0.000000
C	-1.248268	-3.534175	0.000000
H	-1.245477	-4.620958	0.000000
C	-2.436551	-2.848120	0.000000
H	-3.379129	-3.389093	0.000000

Energy = -921.9167349 Hartree

Low Frequencies (cm^{-1}) : 90.278 90.278 129.725 167.010 231.250 302.631

2. TD-DFT results TBP (**1),** Benzene (**2**) and Coronene (**3**) at B3LYP/6-31+G(D,P) level of theory.

(a) **TBP molecule (1)**

Excited State 1: Singlet-A1 2.8820 eV 430.20 nm f=0.0232

HOMO-1 -> LUMO -0.28094

HOMO -> LUMO+1 0.64288

Excited State 2: Singlet-B2 3.0817 eV 402.32 nm f=0.3565

HOMO-1 -> LUMO+1 0.23049

HOMO -> LUMO 0.65719

Excited State 3: Singlet-A1 3.4681 eV 357.50 nm f=0.1398

HOMO-1 -> LUMO 0.63597

HOMO -> LUMO+1 0.27992

Excited State 4: Singlet-B2 3.6456 eV 340.09 nm f=0.4559

HOMO-1 -> LUMO+1 0.65408

HOMO -> LUMO -0.21881

Excited State 5: Singlet-A1 3.LUMO+147 eV 314.31 nm f=0.0027

HOMO-2 -> LUMO 0.32934

HOMO -> LUMO+2 0.60000

Excited State 6: Singlet-B2 3.9736 eV 312.02 nm f=0.0015

HOMO -> LUMO+3 0.66529

HOMO -> LUMO+4 -0.19656

Excited State 7: Singlet-B2 4.1342 eV 299.90 nm f=0.0108

HOMO-5 -> LUMO -0.24366

HOMO-2 -> LUMO+1 0.40064

HOMO-1 -> LUMO+2 0.29972

HOMO -> LUMO+3 -0.18337

HOMO -> LUMO+4 -0.37593

Excited State 8: Singlet-A1 4.2991 eV 288.39 nm f=0.0006

HOMO-4 -> LUMO+1 0.48788

HOMO-3 -> LUMO 0.26634

HOMO-2 -> LUMO 0.16759

HOMO-1 -> LUMO+4 -0.36942

HOMO -> LUMO+5 -0.10726

Excited State 9: Singlet-B2 4.3101 eV 287.66 nm f=0.0123

HOMO-4 -> LUMO 0.66581

HOMO-3 -> LUMO+1 -0.16653

Excited State 10: Singlet-A1 4.3806 eV 283.03 nm f=0.0033

HOMO-5 -> LUMO+1 0.16463

HOMO-4 -> LUMO+1 -0.22257

HOMO-3 -> LUMO 0.45989

HOMO-2 -> LUMO 0.24978

HONO-1 -> LUMO+3 0.23465

HOMO -> LUMO+2 -0.12234

HOMO -> LUMO+5 -0.25788

Excited State 11: Singlet-B2 4.3917 eV 282.31 nm f=0.0933

HOMO-5 -> LUMO 0.14261

HOMO-2 -> LUMO+1 0.39444

HOMO-1 -> LUMO+2 0.25497

HOMO -> LUMO+4 0.48324

Excited State 12: Singlet-A1 4.4370 eV 279.43 nm f=0.0133

HOMO-5 -> LUMO+1 0.14040

HOMO-3 -> LUMO -0.37478

HOMO-2 -> LUMO 0.47152

HOMO-1 -> LUMO+4 -0.14687

HOMO -> LUMO+2 -0.27952

Excited State 13: Singlet-B2 4.4692 eV 277.42 nm f=0.0001

HOMO-4 -> LUMO 0.13159

HOMO-3 -> LUMO+1 0.66303

HOMO -> LUMO+4 -0.12018

Excited State 14: Singlet-A1 4.6314 eV 267.70 nm f=0.0000

HOMO-5 -> LUMO+1 0.12605

HOMO-4 -> LUMO+1 0.16689

HOMO-3 -> LUMO 0.19560

HOMO-1 -> LUMO+3 0.21776

HOMO-1 -> LUMO+4 -0.13056

HOMO -> LUMO+5 0.58460

Excited State 15: Singlet-B2 4.6888 eV 264.43 nm f=0.4757

HOMO-5 -> LUMO 0.51151

HOMO-6 -> LUMO+1 -0.17042

HOMO-1 -> LUMO+2 0.38727

HOMO -> LUMO+4 -0.19661

Excited State 16: Singlet-B2 4.7180 eV 262.79 nm f=0.6487

HOMO-5 -> LUMO -0.36381

HOMO-4 -> LUMO 0.15633

HOMO-2 -> LUMO+1 -0.33775

HOMO-1 -> LUMO+2 0.40967

HOMO -> LUMO+4 0.12584

Excited State 17: Singlet-A1 4.7286 eV 262.20 nm f=0.0003

HOMO-5 -> LUMO+1 0.58567

HOMO-1 -> LUMO+4 0.34452

Excited State 18: Singlet-B1 4.79LUMO+3 eV 258.32 nm f=0.0000

HOMO -> LUMO+6 0.60827

HOMO ->LUMO+8 -0.33912

Excited State 19: Singlet-A1 4.8404 eV 256.15 nm f=0.1663

HOMO-5 -> LUMO+1 -0.11249

HOMO-4 -> LUMO+1 0.32856

HOMO-1 -> LUMO+3 0.46442

HOMO-1 -> LUMO+4 0.34062

HOMO -> LUMO+5 -0.13957

Excited State 20: Singlet-B1 4.LUMO+275 eV 250.10 nm f=0.0013

HOMO -> LUMO+6 0.34257

HOMO ->LUMO+8 0.60568

Excited State 21: Singlet-A2 4.LUMO+459 eV 249.17 nm f=0.0000

HOMO-1 -> LUMO+6 -0.12107

HOMO ->LUMO+7 0.68941

HOMO ->LUMO+9 -0.10251

Excited State 22: Singlet-B2 5.1404 eV 241.20 nm f=0.0007

HOMO-6 -> LUMO 0.14317

HOMO-1 -> LUMO+5 0.62712

HOMO ->LUMO+12 -0.21370

Excited State 23: Singlet-A1 5.1584 eV 240.35 nm f=0.0278

HOMO-7 -> LUMO -0.13018

HOMO-4 -> LUMO+2 0.11290

HOMO-1 -> LUMO+4 -0.25871

HOMO ->LUMO+11 0.58627

Excited State 24: Singlet-A2 5.2026 eV 238.31 nm f=0.0000

HOMO-1 ->LUMO+8 -0.12999

HOMO ->LUMO+7 0.10780

HOMO ->LUMO+9 0.67687

Excited State 25: Singlet-A1 5.2047 eV 238.21 nm f=0.1068

HOMO-7 -> LUMO -0.10238

HOMO-6 -> LUMO+1 0.45590

HOMO-5 -> LUMO+1 -0.16943

HOMO-4 -> LUMO+1 -0.11023

HOMO-3 -> LUMO+3 -0.15967

HOMO-2 -> LUMO 0.14220

HOMO-2 -> LUMO+3 0.15260

HOMO-2 -> LUMO+4 0.94167

HOMO-1 -> LUMO+3 -0.94099

HOMO-1 -> LUMO+4 0.26443

HOMO -> LUMO+5 0.10749

HOMO ->LUMO+11 0.20860

Excited State 26: Singlet-B2 5.2461 eV 236.33 nm f=0.0053

HOMO-6 -> LUMO 0.51790

HOMO-1 -> LUMO+5 -0.25375

HOMO ->LUMO+12 -0.39240

Excited State 27: Singlet-B1 5.2LUMO+46 eV 234.04 nm f=0.0011

HOMO-1 ->LUMO+7 0.13035

HOMO ->LUMO+8 0.10116

HOMO ->LUMO+10 0.67456

Excited State 28: Singlet-A2 5.3766 eV 230.60 nm f=0.0000

HOMO-1 -> LUMO+6 0.66198

HOMO-1 ->LUMO+8 0.17922

HOMO ->LUMO+7 0.11923

Excited State 29: Singlet-A1 5.4083 eV 229.25 nm f=0.0355

HOMO-5 -> LUMO+2 -0.10704

HOMO-4 -> LUMO+2 0.46982

HOMO-3 -> LUMO+3 -0.15638

HOMO-2 -> LUMO+3 0.33224

HOMo-1 -> LUMO+4 -0.12108

HOMO-1 ->LUMO+12 -0.10193

HOMO ->LUMO+11 -0.24741

Excited State 30: Singlet-A1 5.4352 eV 228.11 nm f=0.0644

HOMO-6 -> LUMO+1 0.37446

HOMO-5 -> LUMO+1 0.13098

HOMo-5 -> LUMO+2 -0.24098

HOMO-2 -> LUMO+3 -0.32388

HOMo-2 -> LUMO+4 0.12961

HOMO-1 -> LUMO+3 0.10641

HOMO-1 -> LUMO+4 -0.18653

HOMo-1 ->LUMO+12 -0.17331

(b) Benzene (2)

Excited State 1: Singlet 5.5348 eV 224.01 nm f=0.0000

HOMO-1 -> LUMO 0.49980

HOMO -> LUMO+1 0.49980

Excited State 2: Singlet 6.3020 eV 196.74 nm f=0.0000

HOMO-1 -> LUMO+1 -0.49832

HOMO -> LUMO 0.49832

Excited State 3: Singlet 7.3644 eV 168.36 nm f=0.5583

HOMO-1 -> LUMO+1 0.49801

HOMO -> LUMO 0.49801

Excited State 4: Singlet 7.3644 eV 168.36 nm f=0.5583

HOMO-1 -> LUMO 0.49801

HOMO -> LUMO+1 -0.49801

Excited State 5: Singlet 7.8323 eV 158.30 nm f=0.0000

HOMO-3 -> LUMO+1 -0.49855

HOMO-2 -> LUMO 0.49855

Excited State 6: Singlet 7.9397 eV 156.16 nm f=0.0000

HOMO-3 -> LUMO -0.49875

HOMO-2 -> LUMO+1 0.49877

Excited state symmetry could not be determined.

Excited State 7: Singlet 7.9397 eV 156.16 nm f=0.0000

HOMO-3 -> LUMO+1 0.49877

HOMO-2 -> LUMO 0.49876

Excited State 8: Singlet 7.9543 eV 155.87 nm f=0.0060

HOMO-3 -> LUMO 0.49915

HOMO-2 -> LUMO+1 0.49912

Excited State 9: Singlet 8.0908 eV 153.24 nm f=0.0000

HOMO -> LUMO+2 0.70509

Excited State 10: Singlet 8.0909 eV 153.24 nm f=0.0000

HOMO-1 -> LUMO+2 0.70509

(c) Coronene (3)

Excited State 1: Singlet 3.1548 eV 393.00 nm f=0.0000

HOMO-1 -> LUMO 0.50076

HOMO -> LUMO+1 0.49693

Excited State 2: Singlet 3.3454 eV 370.62 nm f=0.0389

HOMO-1 -> LUMO+1 -0.37586

HOMO -> LUMO 0.59701

Excited State 3: Singlet 4.0872 eV 303.35 nm f=0.6620

HOMO-3 -> LUMO+2 0.10486

HOMO-2 -> LUMO+3 -0.10290

HOMO-1 -> LUMO -0.48250

HOMO -> LUMO+1 0.48527

Excited State 4: Singlet 4.1294 eV 300.25 nm f=0.6213

HOMO-2 -> LUMO+2 0.11062

HOMO-1 -> LUMO+1 0.58419

HOMO -> LUMO 0.35919

Excited State 5: Singlet 4.1467 eV 298.99 nm f=0.0000

HOMO-2 -> LUMO 0.15925

HOMO -> LUMO+2 0.68124

Excited State 6: Singlet 4.2628 eV 2 90.85 nm f=0.0000

HOMO-3 -> LUMO -0.30378

HOMO-2 -> LUMO+1 -0.14869

HOMO-1 -> LUMO+2 0.30443

HOMO -> LUMO+3 0.52712

Excited State 7: Singlet 4.3731 eV 283.52 nm f=0.0000

HOMO-2 -> LUMO 0.59940

HOMO-1 -> LUMO+3 -0.32758

HOMO -> LUMO+2 -0.14406

Excited State 8: Singlet 4.3824 eV 282.91 nm f=0.0000

HOMO-3 -> LUMO 0.24536

HOMO-2 -> LUMO+1 -0.31417

HOMO-1 -> LUMO+2 0.51935

HOMO -> LUMO+3 -0.25796

Excited State 9: Singlet 4.4810 eV 276.69 nm f=0.0000

HOMO-3 -> LUMO+1 0.26092

HOMO-2 -> LUMO 0.30930

HOMO-1 -> LUMO+3 0.57114

Excited State 10: Singlet 4.5919 eV 270.00 nm f=0.0000

HOMO-3 -> LUMO 0.47264

HOMO-2 -> LUMO+1 0.37989

HOMO-1 -> LUMO+2 0.15994

HOMO -> LUMO+3 0.29708