Does the concept of Clar's aromatic sextet work for dicationic forms of polycyclic aromatic hydrocarbons? – testing the model against charged systems in singlet and triplet state.

by

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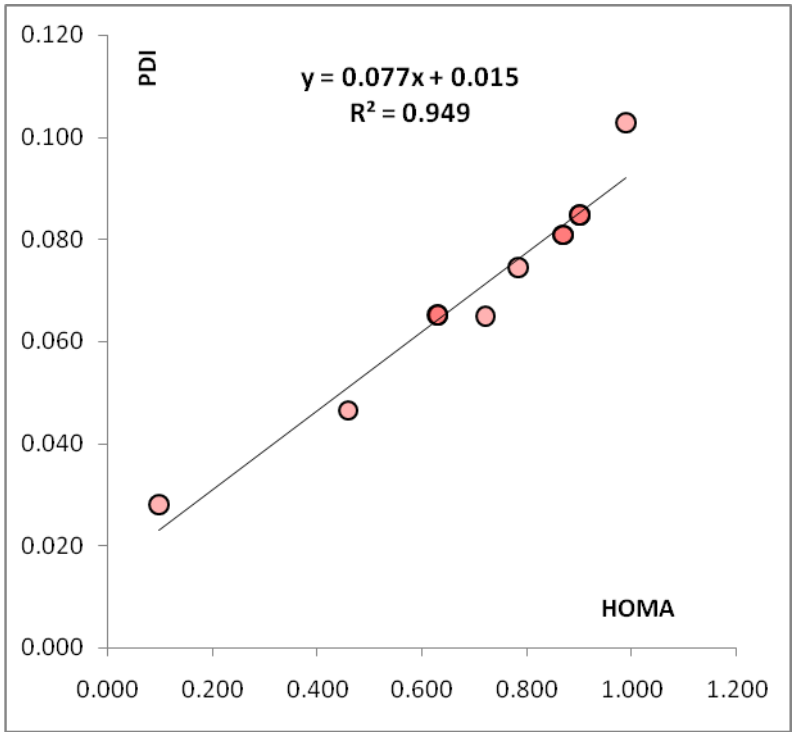
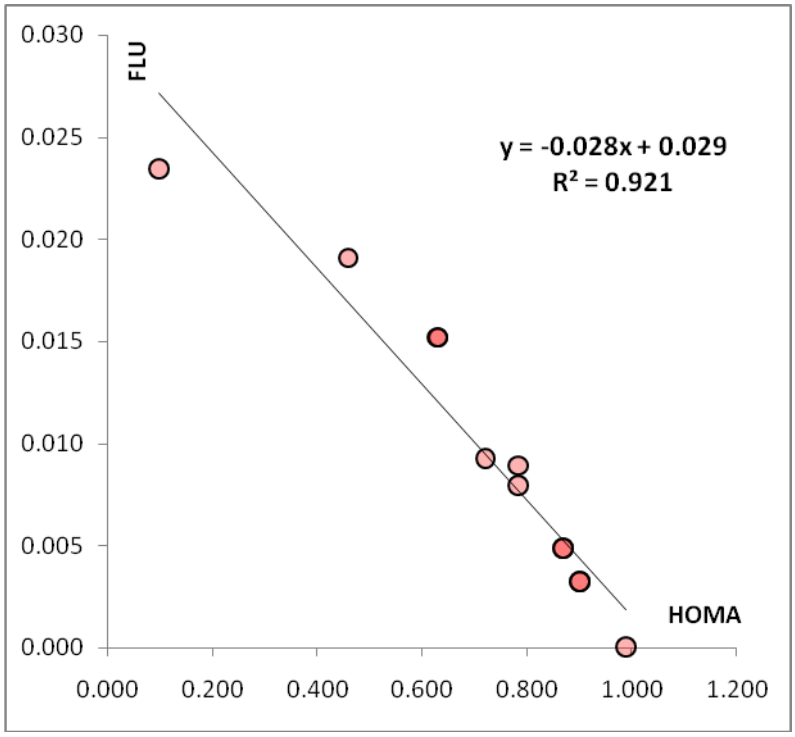
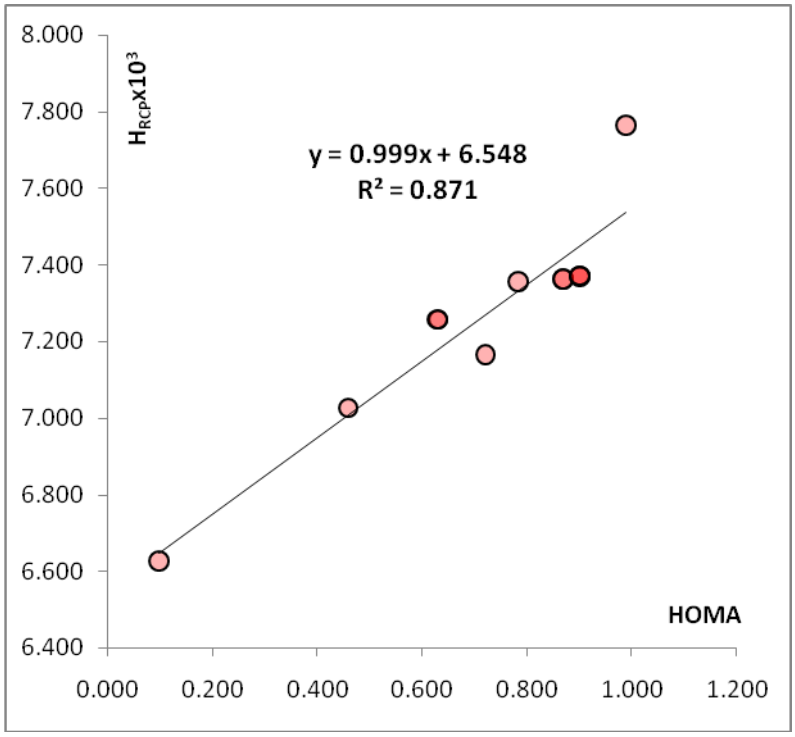
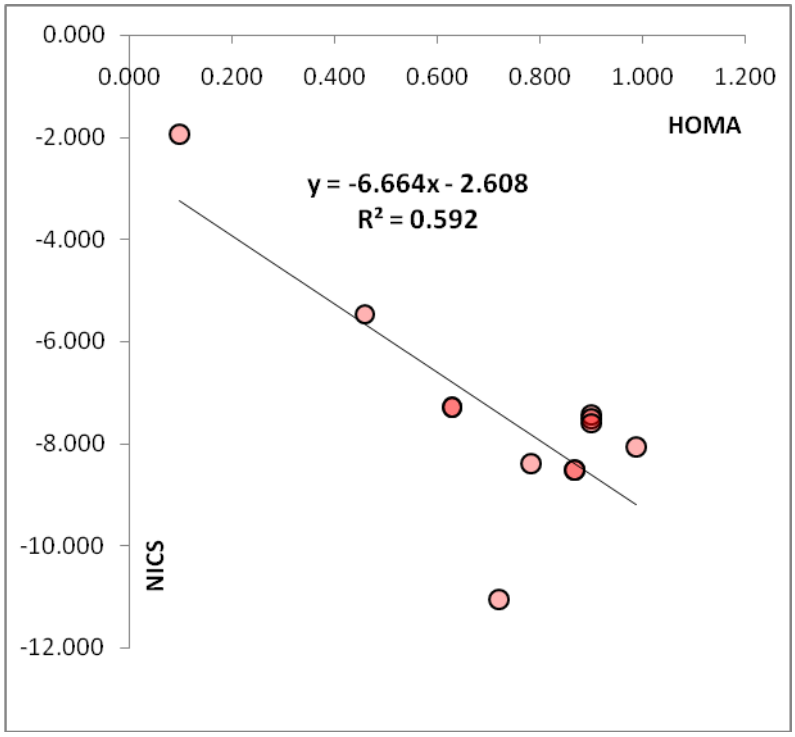
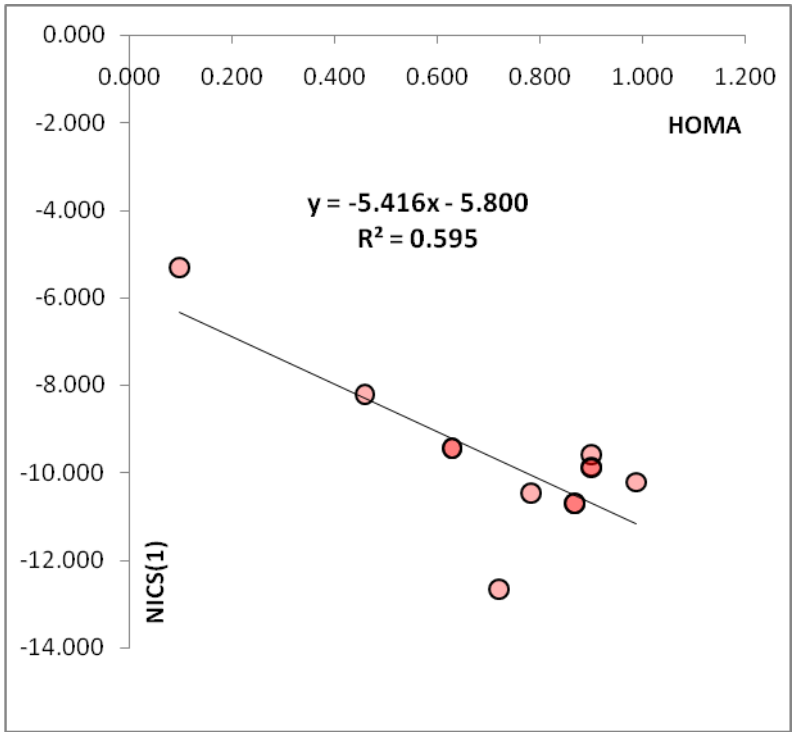
Fig. S1. Diagrams with interrelations between selected aromaticity indices – the case of neutral PAHs.






8.000
7.800
7.600
7.400
7.200
7.000
6.800
6.600
6.400
$H_{RCP}x10^3$
y = 0.999x + 6.548
R^2 = 0.871
HOMA
0.000
0.200
0.400
0.600
0.800
1.000
1.200


0.000
0.000
0.200
0.400
0.600
0.800
1.000
1.200
HOMA
-2.000
-4.000
-6.000
-8.000
-10.000
-12.000
NICS
y = -6.664x - 2.608
R^2 = 0.592


0.000
0.000
0.200
0.400
0.600
0.800
1.000
1.200
HOMA
-2.000
-4.000
-6.000
-8.000
-10.000
-12.000
-14.000
NICS(1)
y = -5.416x - 5.800
R² = 0.595

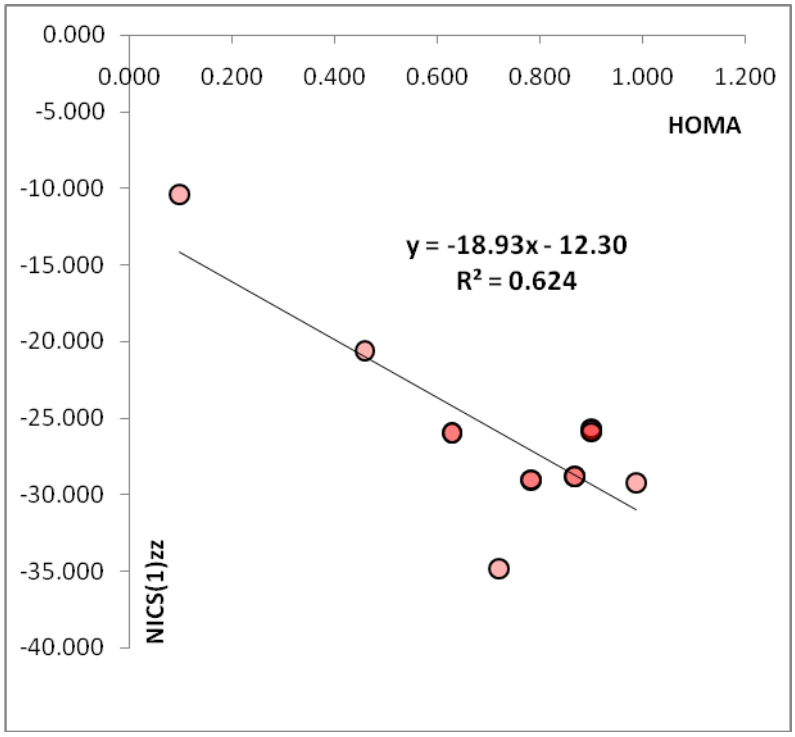
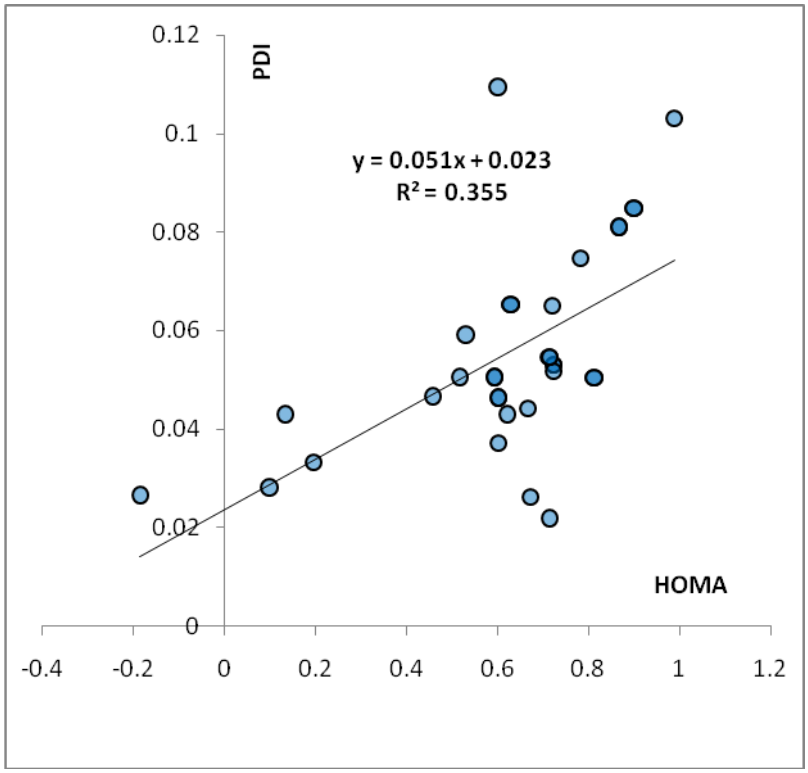
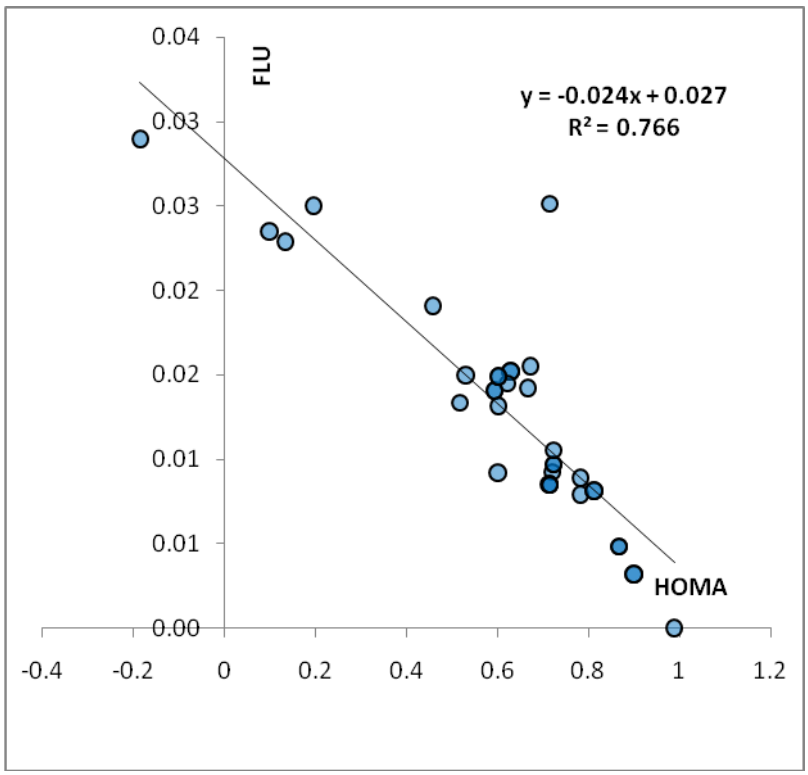
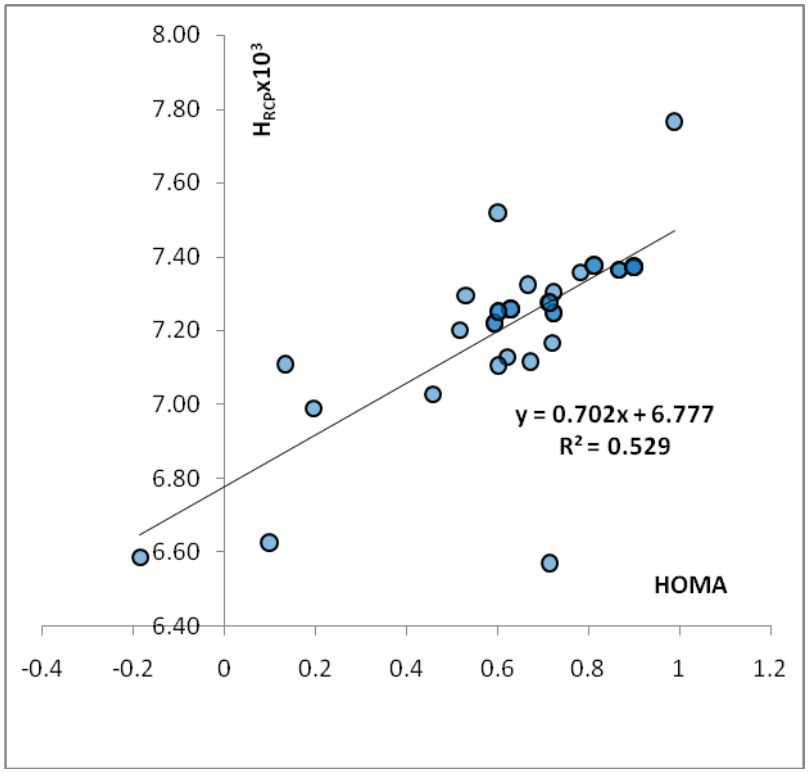
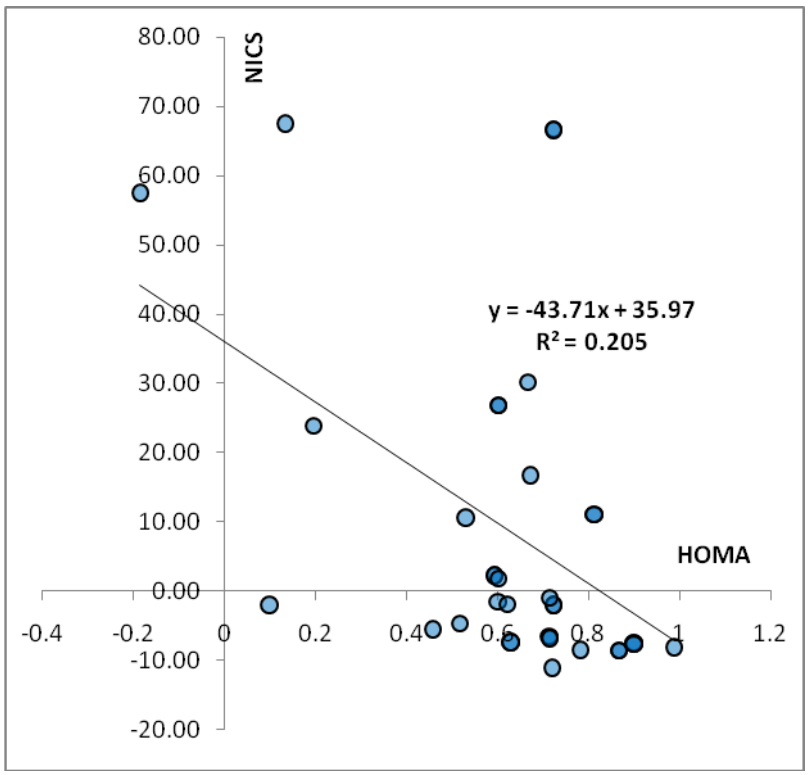

0.000
0.000
0.200
0.400
0.600
0.800
1.000
1.200
HOMA
-5.000
-10.000
-15.000
-20.000
-25.000
-30.000
-35.000
-40.000
NICS(1)zz
y = -18.93x - 12.30
R² = 0.624

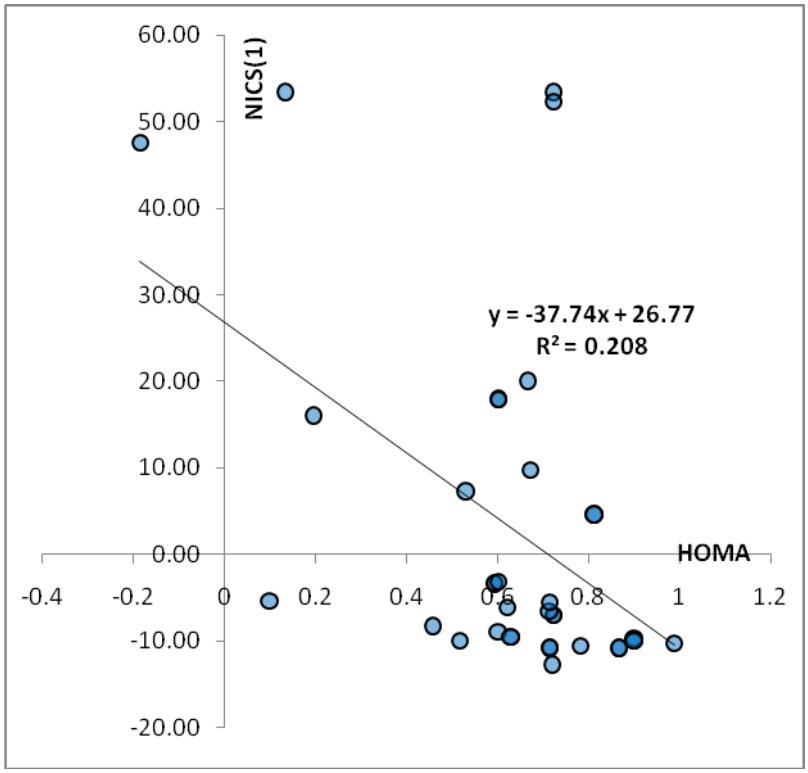
Fig. S2. Diagrams with interrelations between selected aromaticity indices – the case of all systems investigated.






8.00
7.80
7.60
7.40
7.20
7.00
6.80
6.60
6.40
$H_{RCP}x10^3$
y = 0.702x + 6.777
R^2 = 0.529
HOMA
-0.4
-0.2
0
0.2
0.4
0.6
0.8
1
1.2


80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
-10.00
-20.00
NICS
y = -43.71x + 35.97
R^2 = 0.205
HOMA
-0.4
-0.2
0
0.2
0.4
0.6
0.8
1
1.2


NICS(1)
HOMA
y = -37.74x + 26.77
R² = 0.208
60.00
50.00
40.00
30.00
20.00
10.00
0.00
-10.00
-20.00
-0.4
-0.2
0
0.2
0.4
0.6
0.8
1
1.2

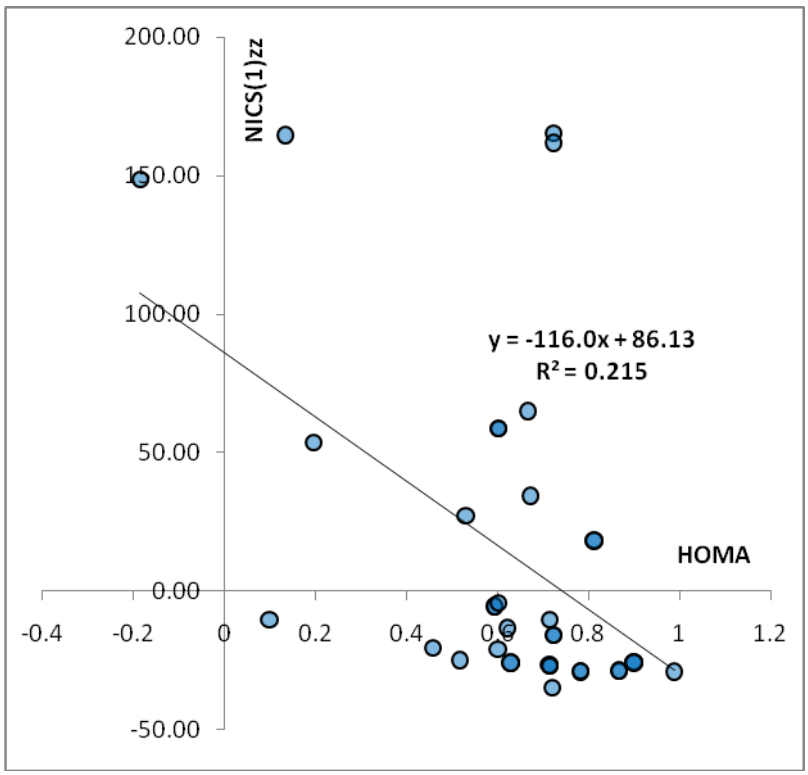
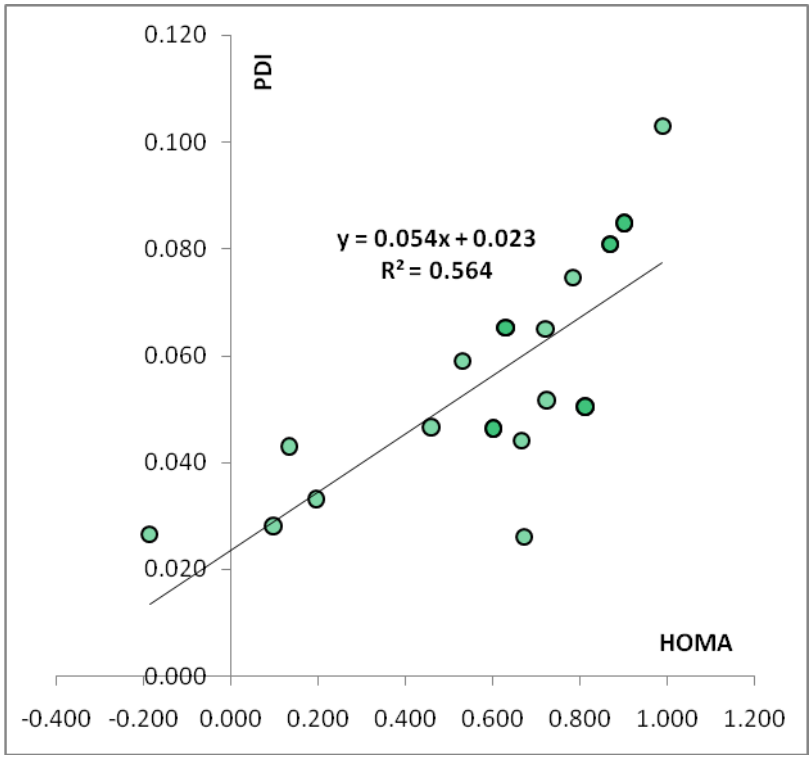
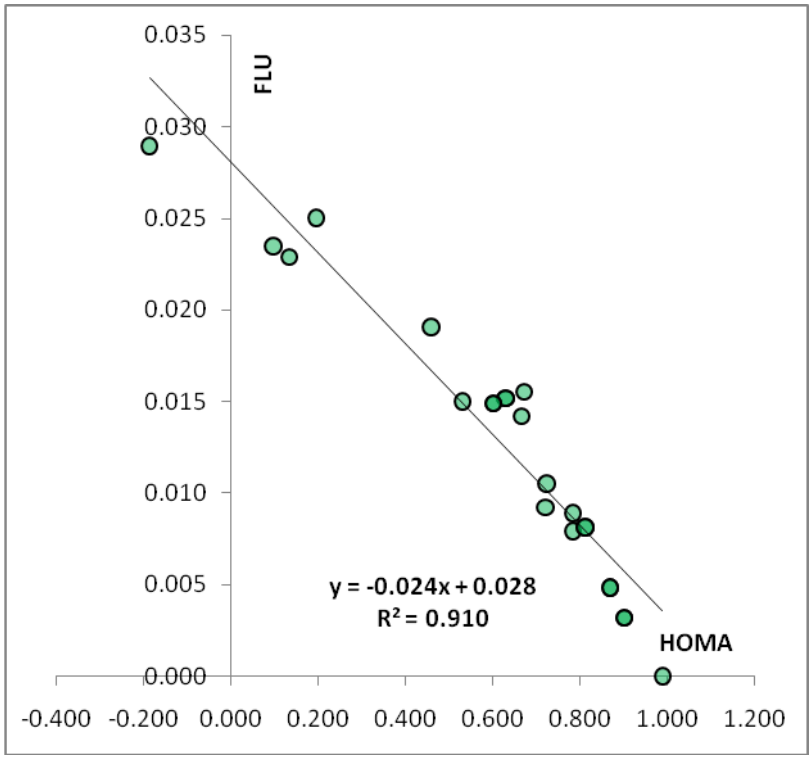
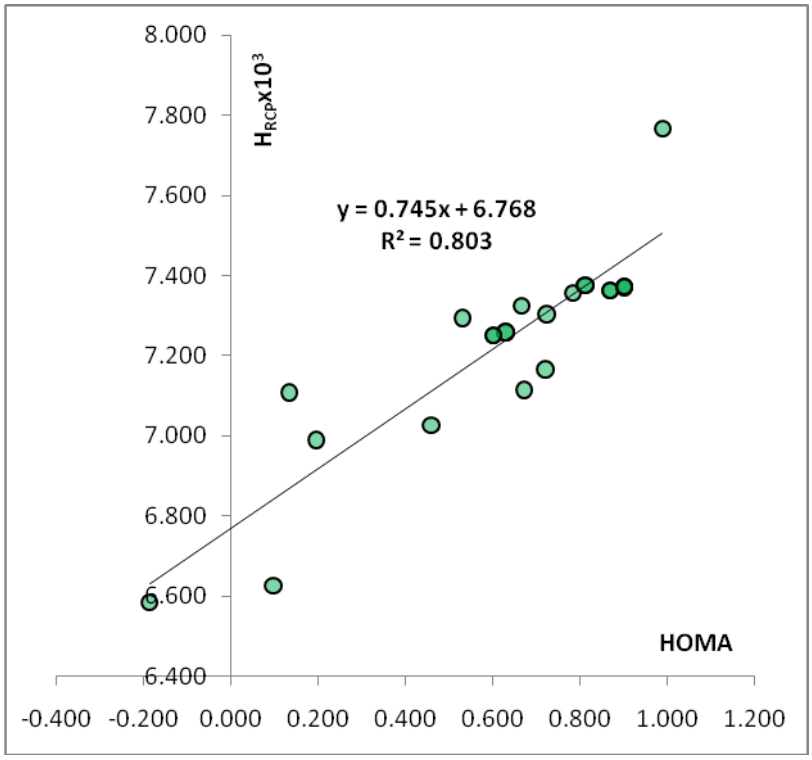
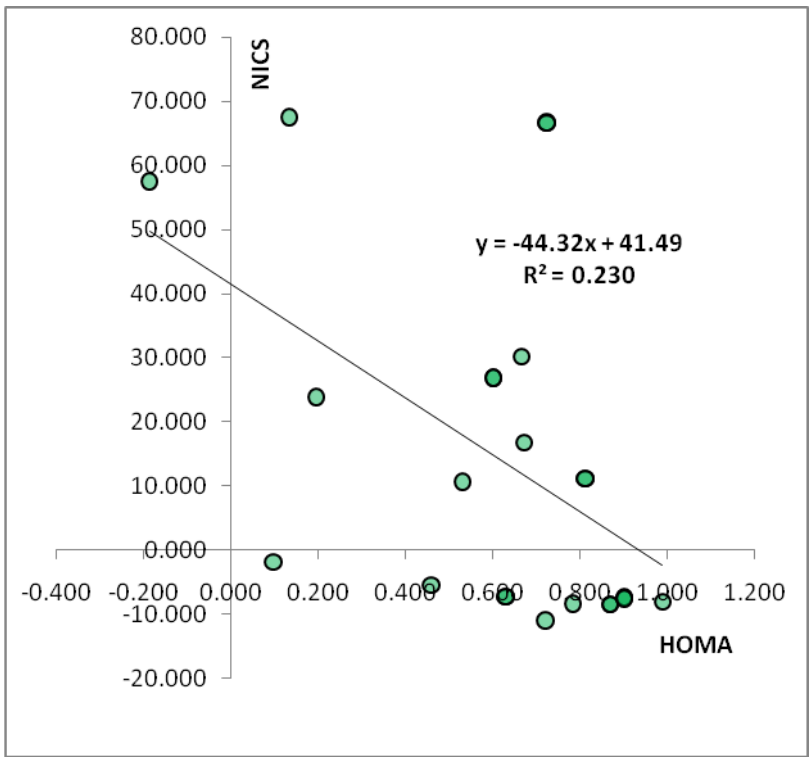

NICS(1)zz
HOMA
y = -116.0x + 86.13
R² = 0.215
200.00
150.00
100.00
50.00
0.00
-50.00
-0.4
-0.2
0
0.2
0.4
0.6
0.8
1
1.2

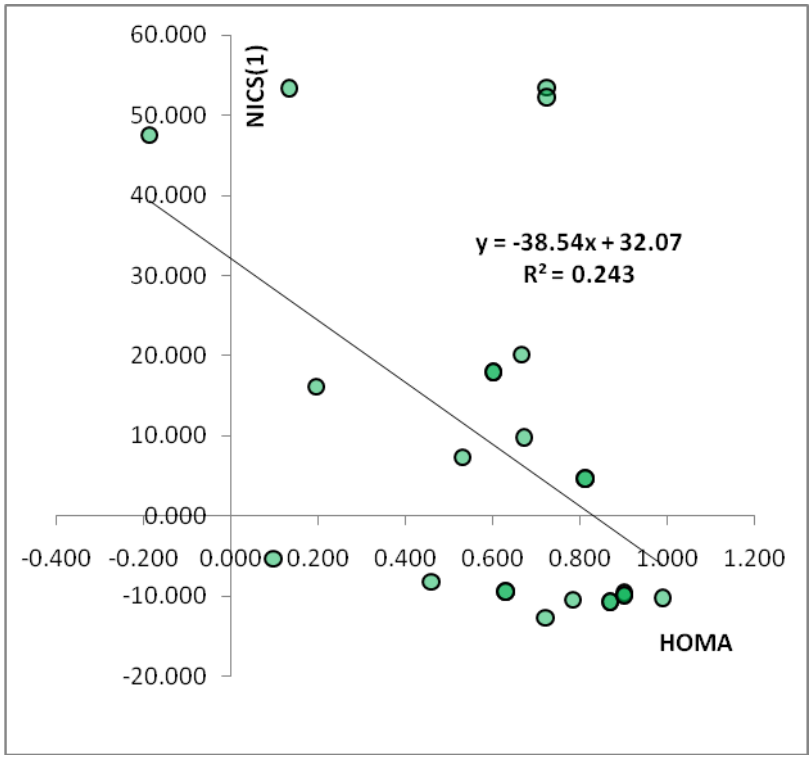
Fig. S3. Diagrams with interrelations between selected aromaticity indices – the case of neutral and singlet state charged PAHs.






8.000
7.800
7.600
7.400
7.200
7.000
6.800
6.600
6.400
$H_{RCP}x10^3$
y = 0.745x + 6.768
R^2 = 0.803
HOMA
-0.400 -0.200 0.000 0.200 0.400 0.600 0.800 1.000 1.200


80.000
70.000
60.000
50.000
40.000
30.000
20.000
10.000
0.000
-10.000
-20.000
NICS
y = -44.32x + 41.49
R^2 = 0.230
HOMA
-0.400 -0.200 0.000 0.200 0.400 0.600 0.800 1.000 1.200


NICS(1)
y = -38.54x + 32.07
R² = 0.243
HOMA
60.000
50.000
40.000
30.000
20.000
10.000
0.000
-10.000
-20.000
-0.400
-0.200
0.000
0.200
0.400
0.600
0.800
1.000
1.200

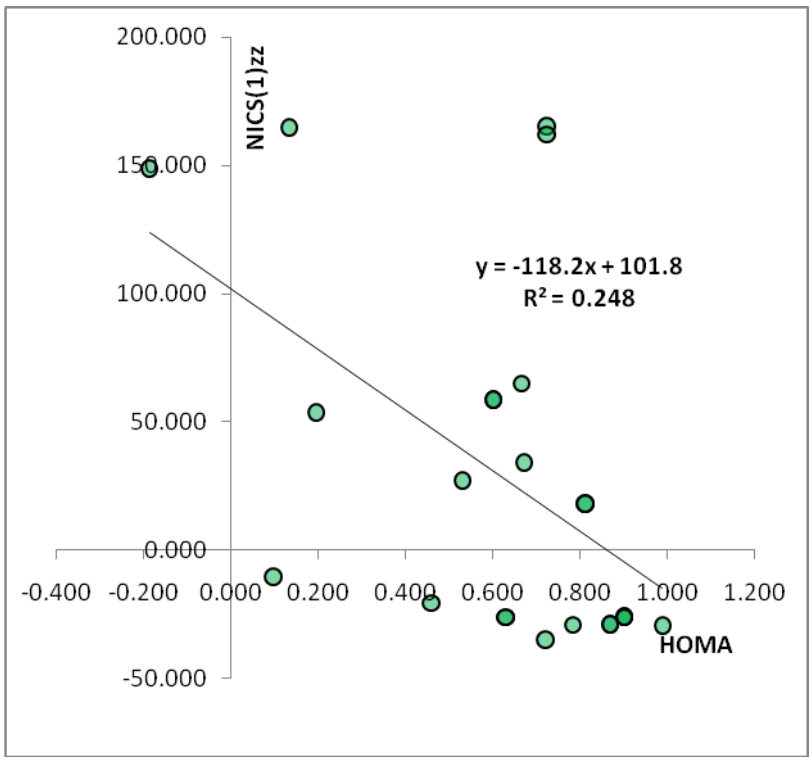

NICS(1)zz
y = -118.2x + 101.8
R² = 0.248
HOMA
200.000
150.000
100.000
50.000
0.000
-50.000
-0.400
-0.200
0.000
0.200
0.400
0.600
0.800
1.000
1.200

Table S1. Optimized geometries of neutral PAHs at B3LYP/6-311++G(d,p) level of theory.

Benzene

C	1.29698700	0.51352500	0.00111200
C	1.09380300	-0.86626000	-0.00245000
C	0.20363400	1.37936900	0.00355900
C	-0.20271800	-1.38020600	-0.00355800
C	-1.29607000	-0.51436200	-0.00111100
C	-1.09288600	0.86542400	0.00244800
H	0.36160600	2.45221200	0.00632700
H	-0.36068700	-2.45304900	-0.00632500
H	2.30508800	0.91313100	0.00197300
H	1.94392200	-1.53949700	-0.00435200
H	-1.94300600	1.53866000	0.00434900
H	-2.30417200	-0.91396600	-0.00197100

E=-232.3112981 a.u.

Naphtalene

C	2.42957900	0.71067000	0.00809700
C	2.43154700	-0.70461300	0.01587800
C	1.24193900	1.40212900	-0.00156900
C	1.24583400	-1.39943500	0.01383700
C	0.00112800	-0.71609600	0.00393700
C	-0.00086300	0.71526400	-0.00393500
C	-1.24557000	1.39860400	-0.01383600
H	-1.24591100	2.48378300	-0.01979400
C	-2.43128200	0.70378100	-0.01587900
C	-2.42931400	-0.71150300	-0.00809900
C	-1.24167500	-1.40296100	0.00156900
H	1.23926500	2.48730400	-0.00754100
H	1.24617600	-2.48461400	0.01979500
H	-1.23899900	-2.48813700	0.00754500
H	-3.37471400	1.23807500	-0.02347100
H	-3.37125600	-1.24846800	-0.00980400
H	3.37152000	1.24763700	0.00979900
H	3.37497700	-1.23890800	0.02346900

E= -385.9889415 a.u.

Anthracene

C	-3.65664800	0.71068700	0.00238200
C	-2.47812900	1.40417800	-0.00030700
C	-1.22277900	0.72096600	-0.00124600
C	-1.22203600	-0.72201800	0.00070700
C	-2.47668200	-1.40651800	0.00349400
C	-0.00103000	1.40210600	-0.00398200
C	0.00041300	-1.40190500	-0.00018600
C	1.22216100	-0.72076500	-0.00292100
C	1.22141800	0.72221900	-0.00487500
C	2.47606500	1.40671900	-0.00766300
H	2.47497800	2.49181600	-0.00913000
C	3.65529600	0.71443700	-0.00847500
C	3.65603000	-0.71048600	-0.00654600
C	2.47751200	-1.40397700	-0.00385800
H	-0.00159000	2.48802200	-0.00545300
H	-2.47816000	2.48927600	-0.00177600
H	-2.47559600	-2.49161500	0.00496000
H	0.00097200	-2.48782100	0.00128200
H	2.47754200	-2.48907600	-0.00238600
C	-3.65591400	-0.71423500	0.00430800
H	4.59958200	1.24718900	-0.01059600
H	4.60086400	-1.24227000	-0.00722800
H	-4.60148100	1.24247100	0.00306500
H	-4.60020000	-1.24698900	0.00643000

E= -539.6603379 a.u.

Phenanthrene

C	3.55700000	-0.29779600	0.01255400
C	2.83462600	0.87627800	0.01358000
C	1.42134600	0.86388900	0.00820900
C	0.72837800	-0.38067600	0.00162200
C	1.49818900	-1.56592900	0.00073900
C	2.87867400	-1.52905900	0.00606200
C	0.67860900	2.09076400	0.00932200
C	-0.72837200	-0.38067500	-0.00386700
C	-1.42136800	0.86389100	-0.00251400
C	-0.67865900	2.09076500	0.00419900
C	-2.83464800	0.87628100	-0.00780800
H	-3.34604100	1.83336600	-0.00668700
C	-3.55699600	-0.29779200	-0.01427900
C	-2.87864100	-1.52905500	-0.01563800
C	-1.49815500	-1.56592700	-0.01054300
H	1.22883300	3.02590700	0.01438300
H	4.64080100	-0.27402000	0.01671900
H	3.34599600	1.83336200	0.01856900
H	1.00620200	-2.52988300	-0.00419400
H	3.44115300	-2.45596900	0.00522400
H	-1.22890500	3.02590900	0.00510100
H	-4.64079700	-0.27401500	-0.01829500
H	-3.44109900	-2.45596500	-0.02071100
H	-1.00614700	-2.52988300	-0.01174700

E= -539.6684853 a.u.

Triphenylene

C	0.40430900	-2.72306100	-0.01719500
C	1.05512700	-1.47001700	-0.01176000
C	0.29972700	-0.21367600	-0.01135900
C	-1.11219400	-0.20089900	-0.01636300
C	2.47340000	-1.44484200	-0.00658100
C	0.98703900	1.02718400	-0.00582100
C	2.45274700	1.05319300	-0.00059800
C	3.18370300	-0.16249100	-0.00094000
C	3.16977200	2.26955300	0.00482300
C	0.22725700	2.21734000	-0.00550300
C	-1.15359000	2.20201200	-0.01044800
C	-1.83167600	0.97780400	-0.01596200
H	-2.91540000	0.95077400	-0.01989200
H	-1.70553000	3.13505400	-0.01004100
C	1.10798900	-3.91126800	-0.01755300
C	2.50723100	-3.88643300	-0.01240700
C	3.16829100	-2.67401000	-0.00705200
H	0.57591100	-4.85576800	-0.02179800
H	3.07249700	-4.81146300	-0.01260800
C	4.59427800	-0.09957900	0.00420400
C	4.55029000	2.30328500	0.00978400
H	5.06873700	3.25533600	0.01387100
C	5.27143700	1.10392400	0.00948300
H	6.35543800	1.11537900	0.01334300
H	-1.66036200	-1.13260400	-0.02065700
H	-0.67566500	-2.77033100	-0.02122700
H	4.24926200	-2.68294500	-0.00314800
H	5.17521600	-1.01122500	0.00406400
H	2.63698700	3.21014300	0.00514500
H	0.72625700	3.17628900	-0.00128400

E= -693.3446763 a.u.

Table S2. Optimized geometries of charged PAHs at B3LYP/6-311++G(d,p) level of theory.

Benzene^{2+} (singlet state)

C	1.39425100	0.55282900	-0.27677000
C	1.09286700	-0.77366600	0.01766100
C	0.26640300	1.31117900	0.02319400
C	-0.26548500	-1.31201400	-0.02319400
C	-1.39333500	-0.55366500	0.27677300
C	-1.09195000	0.77282800	-0.01766100
H	0.39487200	2.32273400	0.43335400
H	-0.39395900	-2.32356800	-0.43335600
H	2.40405100	0.95311100	-0.27289700
H	1.88025800	-1.42434900	0.42337700
H	-1.87934000	1.42351000	-0.42338000
H	-2.40313300	-0.95395000	0.27289900

E= -231.4099416 a.u.

Benzene^{2+} (triplet state)

C	1.32546600	0.52491800	-0.03693700
C	1.11784100	-0.88538700	0.03533500
C	0.20810800	1.40959100	0.04157500
C	-0.20719100	-1.41042800	-0.04157500
C	-1.32455000	-0.52575500	0.03693700
C	-1.11692400	0.88455000	-0.03533500
H	0.36613300	2.48228000	0.15317400
H	-0.36521700	-2.48311700	-0.15317400
H	2.33366300	0.92485900	-0.14499400
H	1.96809400	-1.55898900	0.14219100
H	-1.96717800	1.55815200	-0.14219200
H	-2.33274600	-0.92569500	0.14499500

E= -231.4136397 a.u.

Naphtalene2+ (singlet state)

C	2.47440500	0.68940500	0.00833300
C	2.47631500	-0.68321800	0.01580800
C	1.22691800	1.40400100	-0.00164500
C	1.23082100	-1.40134900	0.01363000
C	0.00112700	-0.71553700	0.00389300
C	-0.00086300	0.71470500	-0.00389300
C	-1.23055600	1.40051600	-0.01363000
H	-1.24851200	2.48769400	-0.01962800
C	-2.47605100	0.68238500	-0.01580900
C	-2.47414100	-0.69023800	-0.00833200
C	-1.22665400	-1.40483300	0.00164500
H	1.24184800	2.49122600	-0.00748300
H	1.24877600	-2.48852700	0.01962800
H	-1.24158400	-2.49205800	0.00748200
H	-3.40737700	1.23887800	-0.02338400
H	-3.40391500	-1.24936900	-0.00983000
H	3.40418000	1.24853700	0.00983200
H	3.40764100	-1.23971100	0.02338300

E= -385.2127427 a.u.

Naphtalene^{2+} (triplet state)

C	2.43679900	0.71923200	0.00807200
C	2.43879200	-0.71315400	0.01591200
C	1.22988200	1.43004500	-0.00176100
C	1.23385600	-1.42738500	0.01387800
C	0.00115900	-0.73848200	0.00403800
C	-0.00089400	0.73764900	-0.00404000
C	-1.23359200	1.42655300	-0.01387900
H	-1.24843600	2.51200500	-0.01988800
C	-2.43852700	0.71232200	-0.01591000
C	-2.43653500	-0.72006500	-0.00807100
C	-1.22961800	-1.43087700	0.00176000
H	1.24170800	2.51553500	-0.00763700
H	1.24870000	-2.51283800	0.01988400
H	-1.24144400	-2.51636700	0.00763600
H	-3.38567800	1.24342700	-0.02347700
H	-3.38220500	-1.25385300	-0.00981100
H	3.38246900	1.25302100	0.00981200
H	3.38594200	-1.24425900	0.02348400

E= -385.1956228 a.u.

Anthracene^{2+} (singlet state)

C	-3.67857400	0.69151700	0.00248700
C	-2.45817200	1.40531000	-0.00034400
C	-1.23400800	0.71873200	-0.00122900
C	-1.23326800	-0.71979600	0.00077500
C	-2.45672300	-1.40762900	0.00357500
C	-0.00103500	1.40915700	-0.00404600
C	0.00041700	-1.40895600	-0.00012100
C	1.23339100	-0.71853100	-0.00293800
C	1.23265000	0.71999700	-0.00494200
C	2.45610600	1.40783000	-0.00774200
H	2.46992500	2.49300400	-0.00927400
C	3.67724200	0.69528800	-0.00858500
C	3.67795600	-0.69131600	-0.00665300
C	2.45755500	-1.40511000	-0.00382300
H	-0.00159400	2.49597000	-0.00556000
H	-2.47310700	2.49046900	-0.00183300
H	-2.47054200	-2.49280300	0.00510800
H	0.00097600	-2.49577000	0.00139300
H	2.47249000	-2.49026900	-0.00233400
C	-3.67786000	-0.69508700	0.00441900
H	4.61356500	1.24172900	-0.01075500
H	4.61484200	-1.23679700	-0.00730000
H	-4.61545900	1.23699700	0.00313400
H	-4.61418300	-1.24152800	0.00658800

E= -538.9684006 a.u.

Anthracene^{2+} (triplet state)

C	-3.67667700	0.67977000	0.00251900
C	-2.46305500	1.41193100	-0.00025400
C	-1.22631900	0.74783700	-0.00123100
C	-1.22064300	-0.70142600	0.00066300
C	-2.48329800	-1.41526800	0.00348600
C	-0.00105100	1.44227700	-0.00397400
C	0.00040800	-1.39336300	-0.00025300
C	1.22074700	-0.70017400	-0.00298700
C	1.22493100	0.74909300	-0.00489700
C	2.46098300	1.41445500	-0.00762000
H	2.49556400	2.49893000	-0.00909600
C	3.67535800	0.68353800	-0.00847800
C	3.67787500	-0.72821200	-0.00662700
C	2.48413600	-1.41272300	-0.00394000
H	-0.00160900	2.52754700	-0.00539800
H	-2.49875100	2.49637000	-0.00162400
H	-2.46939200	-2.50002200	0.00488700
H	0.00096600	-2.47844800	0.00117100
H	2.47134600	-2.49749000	-0.00249500
C	-3.67774100	-0.73198200	0.00437300
H	4.61598600	1.22452700	-0.01059600
H	4.61925200	-1.26490800	-0.00733000
H	-4.61786100	1.21979400	0.00321700
H	-4.61856500	-1.26964200	0.00648300

E= -538.9320275 a.u.

Phenanthrene^{2+} (singlet state)

C	3.61848100	-0.27021000	0.01287400
C	2.88286100	0.89393100	0.01378400
C	1.43528200	0.85033000	0.00820300
C	0.73768300	-0.42050000	0.00153800
C	1.50782400	-1.56365100	0.00085200
C	2.93258200	-1.48956900	0.00645100
C	0.72230300	2.02783700	0.00931500
C	-0.73767600	-0.42049900	-0.00403900
C	-1.43530400	0.85033100	-0.00253200
C	-0.72235300	2.02783700	0.00392700
C	-2.88288400	0.89393300	-0.00784600
H	-3.37298800	1.86212500	-0.00652200
C	-3.61847700	-0.27020600	-0.01444600
C	-2.93254900	-1.48956500	-0.01586000
C	-1.50779000	-1.56364900	-0.01071900
H	1.23808200	2.98330400	0.01431000
H	4.70129500	-0.24818600	0.01701600
H	3.37294300	1.86212200	0.01868800
H	1.06150900	-2.54980300	-0.00391200
H	3.49421600	-2.41873500	0.00564100
H	-1.23815400	2.98330500	0.00506800
H	-4.70129200	-0.24818100	-0.01846200
H	-3.49416200	-2.41873000	-0.02103200
H	-1.06145200	-2.54980000	-0.01229600

E= -538.9422349 a.u.

Phenanthrene^{2+} (triplet state)

C	3.56314000	-0.31287000	0.01255600
C	2.82971000	0.89143700	0.01364700
C	1.41699100	0.88462700	0.00828300
C	0.71272400	-0.37895000	0.00157100
C	1.49548900	-1.57579900	0.00069200
C	2.89179400	-1.53652500	0.00609200
C	0.70012900	2.09718600	0.00946000
C	-0.71271800	-0.37894900	-0.00381300
C	-1.41701400	0.88462800	-0.00243200
C	-0.70018000	2.09718600	0.00416300
C	-2.82973300	0.89144000	-0.00775400
H	-3.35761100	1.83958400	-0.00671700
C	-3.56313500	-0.31286600	-0.01438600
C	-2.89176100	-1.53652200	-0.01575900
C	-1.49545500	-1.57579800	-0.01060000
H	1.23724100	3.03971700	0.01451400
H	4.64711000	-0.28165700	0.01675300
H	3.35756700	1.83958100	0.01868700
H	1.01518600	-2.54547000	-0.00422900
H	3.45220600	-2.46440500	0.00523400
H	-1.23731400	3.03971900	0.00514800
H	-4.64710600	-0.28165200	-0.01838900
H	-3.45215200	-2.46440100	-0.02084600
H	-1.01513000	-2.54546900	-0.01187500

E= -538.9388381 a.u.

Triphenylene^{2+} (singlet state)

C	0.37005400	-2.70326600	-0.10069300
C	1.01249400	-1.43273000	-0.04482600
C	0.28958800	-0.21741200	-0.04204300
C	-1.15286000	-0.21644900	-0.05223600
C	2.51492000	-1.40606200	0.02657100
C	0.98165800	1.04202300	0.00409700
C	2.45732300	1.06841300	-0.01069000
C	3.19394800	-0.16571100	0.02974800
C	3.16998300	2.25242700	-0.07445400
C	0.22718100	2.19953500	0.07334200
C	-1.18945300	2.16554700	0.06952500
C	-1.87771900	0.95479700	0.00190000
H	-2.96022800	0.93364200	-0.00421500
H	-1.73576200	3.10136800	0.11936200
C	1.08879000	-3.86173600	-0.06558400
C	2.52539800	-3.83632000	0.03563800
C	3.20232100	-2.65311600	0.07635200
H	0.58085600	-4.81846800	-0.11055300
H	3.06716900	-4.77451400	0.07603000
C	4.63544200	-0.11325000	0.04040700
C	4.58692300	2.26906500	-0.07035800
H	5.09945700	3.22402500	-0.11572700
C	5.31800000	1.08337600	-0.00804200
H	6.40057300	1.10087800	-0.00163000
H	-1.69410100	-1.14998000	-0.09687600
H	-0.70450400	-2.76923100	-0.17230600
H	4.27856000	-2.68104100	0.14765100
H	5.20970200	-1.02703500	0.08094200
H	2.66571800	3.20682700	-0.13674600
H	0.69705400	3.17105300	0.13993200

E= -692.6339039 a.u.

Triphenylene^{2+} (triplet state)

C	0.38622700	-2.72178300	-0.01731000
C	1.03552500	-1.46623800	-0.01185100
C	0.29388300	-0.23277100	-0.01144800
C	-1.11953100	-0.21746700	-0.01648800
C	2.49284400	-1.44036400	-0.00651900
C	1.00011900	1.04224300	-0.00570900
C	2.43911900	1.06777300	-0.00060500
C	3.19019600	-0.18136500	-0.00094400
C	3.15907700	2.28419000	0.00480400
C	0.23741600	2.23236400	-0.00533700
C	-1.14799500	2.20514200	-0.01034300
C	-1.83133600	0.97144600	-0.01598600
H	-2.91501100	0.95243900	-0.01992300
H	-1.70671000	3.13388700	-0.00992500
C	1.10252000	-3.90799400	-0.01763800
C	2.51261000	-3.88296400	-0.01244900
C	3.18632500	-2.67209300	-0.00702700
H	0.57755500	-4.85621600	-0.02188600
H	3.07090400	-4.81196300	-0.01270300
C	4.60218600	-0.11588000	0.00426500
C	4.54459500	2.30619300	0.00978500
H	5.06995600	3.25419500	0.01387700
C	5.27132400	1.09754900	0.00953700
H	6.35499100	1.11701400	0.01345600
H	-1.67985200	-1.14060400	-0.02086900
H	-0.69187700	-2.78378600	-0.02137200
H	4.26595200	-2.69580700	-0.00317000
H	5.19495600	-1.01853800	0.00423400
H	2.63977300	3.23101200	0.00514600
H	0.72274700	3.19704700	-0.00108300

E= -692.6384981 a.u.