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# Identification of Carbonium and Carbenium Ions by QTAIM

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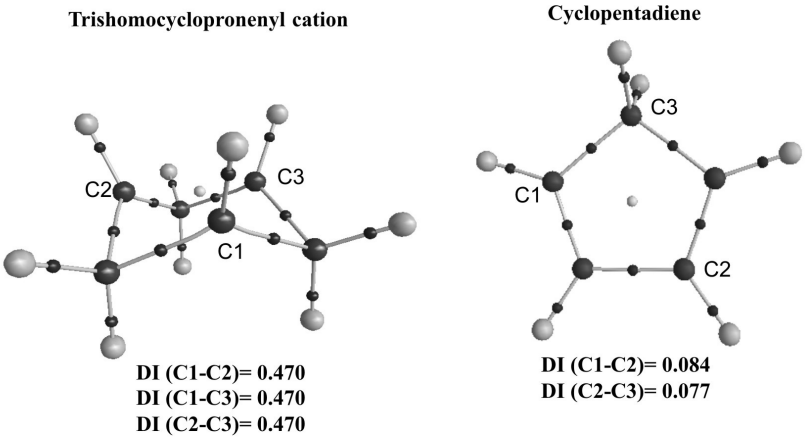
*Delocalization indexes of carbon atoms in trishomocyclopropenyl cation[1] and cyclopentadiene.*




*Bond order and delocalization index*

Matta and Hernandez-Trujillo[3] established a relation between the delocalization index and the bond order. Although the concept of DI is different from the Lewis concept of bond order, the former can be used to estimate the bond order of a covalent bond in an alternative way (See Table S1)

**Table S1.** Bond orders in ethane, ethylene, benzene, hexatriene and anthracene according to Ruedenberg bond order, Coulson bond order, experimental bond order and the delocalization index

| Molecule | Bond | Ruedenberg bond order[a] | Coulson bond order[b] | Experimental bond order[c] | Delocalization index[d] |
|---|---|---|---|---|---|
| Ethane | C-C | 0.00 | - | 1.16 | 1.00 |
| Ethylene | C=C | 1.00 | 2.00 | 1.80 | 1.99 |
| Benzene | CC | - | 1.66 | 1.63 | 1.39 |
| Hexatriene | C=C | 0.85 | 1.87 / 1.78 | - | 1.74 |
| | C-C | 0.38 | 1.48 | - | 1.14 |
| Anthracene | $C_1$-$C_2$ | 0.70 | - | - | 1.48 |
| | $C_2$-$C_3$ | 0.49 | - | - | 1.21 |

[a]From Reference 4; [b]From Reference 5; [c]From Reference 2; [d]Calculated from B3LYP/6-311++G** level of theory.

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*Relation between bond order and charge density*

From the relation between bond order ($n$) and charge density in the BCP of a CC bond ($\rho_b$), $n = \exp[A(\rho_b - B)]$, a plot of the natural logarithm of bond order *versus* charge density of CC bond (Figure 1) from known values of bond order and charge density of BCP from ethane, ethylene, acetylene and benzene (Table S2) was constructed (Figure S1). The values of charge density in the bond critical points of CC bonds of ethane, benzene, ethylene and acetylene were obtained by B3LYP/6-311++G** level.

**Table S2.:** Charge density of CC bonds and natural logarithm of bond order of the corresponding CC bonds of ethane, benzene, ethylene and acetylene

| Molecule | $\rho_b$ | ln $n$ |
|---|---|---|
| Ethane | 0.231 | 0 |
| Benzene | 0.309 | 0.470 |
| Ethylene | 0.344 | 0.693 |
| Acetylene | 0.412 | 1.098 |

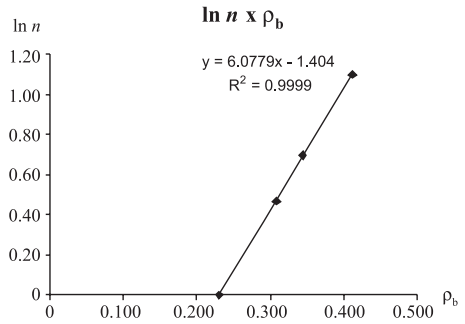


**Figure S1.** Natural logarithm of bond order x charge density of CC bond plot.

## References

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*Comparison of delocalization indexes between MP2 and B3LYP*

DI (C-C) = 1.379 (B3LYP)
DI (C-C) = 1.364 (MP2)

DI (C-C) = 1.437 (B3LYP)
DI (C-C) = 1.432 (MP2)

*Computed energy values of systems **1** to **9** and cyclopentene*

| Entry | H (Hartree) | S (cal mol$^{-1}$ K$^{-1}$) | G (Hartree) |
|---|---|---|---|
| 1 | –194.342783 | 70.986 | –194.376511 |
| 2 | –425.416761 | 93.573 | –425.461220 |
| 3 | –426.624261 | 89.761 | –426.666910 |
| 4 | –502.797730 | 99.115 | –502.844823 |
| 5 | –617.335286 | 111.430 | –617.388230 |
| 6 | –839.926255 | 120.742 | –839.983623 |
| 7 | –504.023172 | 99.509 | –504.070452 |
| 8 | –618.561144 | 111.806 | –618.614267 |
| 9 | –841.151291 | 120.986 | –841.208776 |
| Cyclopentene | –195.260159 | 69.448 | –195.293156 |

*Internal coordinates of optimized structures*

*Structure 1*

Charge = 1 Multiplicity = 1
C,0,0.0319640497,-0.1165705013,0.0365149283
C,0,0.1138490774,0.1965866624,1.4473079245
C,0,1.4387591539,-0.11676445,1.9389268773
C,0,2.1867708038,-0.646219493,0.746396755
C,0,1.3915516007,-0.6453337358,-0.3295296022
H,0,-0.6965298635,0.6043902691,2.0466052335
H,0,-0.3139606236,0.7786545606,-0.5216318108
H,0,1.8710739475,0.7790686748,2.4322221061
H,0,1.3551312288,-0.8016563921,2.8089938527
H,0,-0.8239769529,-0.8022051186,-0.1380366532
H,0,1.6484435404,-0.9685893282,-1.3281267504
H,0,3.2166584045,-0.9699582278,0.7933532687

*Structure 2*

Charge = 1 Multiplicity = 1
C,0,0.1389914862,0.4919166781,0.2870062019
C,0,0.0637158449,-0.4217152039,1.2508833793
C,0,1.4320362964,-0.9143958226,1.6481969204
C,0,2.3751555522,-0.1535790487,0.7670939294
C,0,1.5692701967,0.7533684384,-0.1113784003
H,0,1.6635963137,-0.7363512234,2.7087913028
H,0,1.5590865996,-1.9979232798,1.5079774509
H,0,1.8727801955,1.8009115226,0.0326556657
H,0,1.7675426581,0.5438225247,-1.1727700086
C,0,3.7762902728,-0.271830474,0.7654683258
C,0,4.5738263982,0.5065372269,-0.1262997936
C,0,4.4331175982,-1.1744936969,1.6548625928
C,0,5.9472687492,0.384278458,-0.1253438325
H,0,4.1003428111,1.1990845543,-0.8105190736
C,0,5.8071938856,-1.2890388696,1.6475184772
H,0,3.8506160756,-1.7750259293,2.3419242872
C,0,6.5638435918,-0.5117040901,0.759249906
H,0,6.5491451601,0.9760709104,-0.8034726146
H,0,6.3020814294,-1.975227767,2.3232150885
H,0,7.6441731707,-0.6049751897,0.7566310664
H,0,-0.840429668,-0.7900890932,1.7156214226
H,0,-0.6926937162,1.0039129087,-0.1770376729

*Structure 3*

C
C,1,B1
C,2,B2,1,A1
C,3,B3,2,A2,1,D1,0
C,4,B4,3,A3,2,D2,0
H,1,B5,2,A4,3,D3,0
H,1,B6,2,A5,3,D4,0
H,2,B7,1,A6,5,D5,0
H,2,B8,1,A7,5,D6,0
H,3,B9,2,A8,1,D7,0
H,3,B10,2,A9,1,D8,0
H,5,B11,4,A10,3,D9,0
H,5,B12,4,A11,3,D10,0
C,4,B13,3,A12,2,D11,0
C,14,B14,4,A13,3,D12,0
C,14,B15,4,A14,3,D13,0
C,15,B16,14,A15,4,D14,0
H,15,B17,14,A16,4,D15,0
C,16,B18,14,A17,4,D16,0
H,16,B19,14,A18,4,D17,0
C,19,B20,16,A19,14,D18,0
H,17,B21,15,A20,14,D19,0
H,19,B22,16,A21,14,D20,0
H,21,B23,19,A22,16,D21,0

Variables:
B1=1.54916997
B2=1.54179207
B3=1.50293595
B4=1.50377255
B5=1.08972001
B6=1.09101639
B7=1.0910065
B8=1.08954835
B9=1.09416146
B10=1.09899061
B11=1.09836181
B12=1.0941379
B13=1.40998211
B14=1.42982174
B15=1.43166926
B16=1.37766245
B17=1.08119659
B18=1.37828826
B19=1.08063491
B20=1.40173673
B21=1.08251018
B22=1.08257209
B23=1.08466603
A1=106.78964547
A2=108.26651082
A3=109.17290882
A4=110.93170715
A5=111.13352678
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A7=111.17528373
A8=111.61451136
A9=112.78295556
A10=108.29526981
A11=111.54882883
A12=125.18332048
A13=120.76150898
A14=121.49859125
A15=120.98161736
A16=119.74157398
A17=121.00292024
A18=119.91665798
A19=119.45280271
A20=120.64322935
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A22=119.37542955
D1=-7.32111319

D2=3.56055099
D3=129.18974784
D4=-112.25870742
D5=-112.16460935
D6=129.28114643
D7=114.77422199
D8=-128.07813816
D9=124.30883401
D10=-121.58438324
D11=-175.60248684
D12=-4.59514491
D13=175.10614424
D14=-178.88719263
D15=-1.53687308
D16=-178.84584935
D17=-1.41218403
D18=-2.09252437
D19=177.28697745
D20=177.45687286
D21=-178.94781261

*Structure 4*

Charge = 1 Multiplicity = 1
C,0,0.9921341728,0.3475202426,-0.1213362462
C,0,0.1421470419,0.2251274832,1.1388567634
C,0,2.3036649391,-0.295538475,1.6932482836
C,0,2.2683866522,0.039676734,0.205986329
C,0,1.2833451421,0.7876515049,1.9525933893
C,0,0.0592853535,-1.2615923077,1.5899941501
H,0,-0.6086994103,-1.3554992457,2.4480747424
H,0,-0.3390639276,-1.8826384218,0.7876918736
C,0,1.5251151439,-1.6144909019,1.9662882159
H,0,1.6137363781,-1.88976421,3.0187226021
H,0,1.9359370988,-2.430740171,1.3721451183
H,0,-0.7969800593,0.768680554,1.116204361
H,0,3.2794868102,-0.2127663492,2.1611610566
H,0,0.6231274058,0.6885303272,-1.0803192878
H,0,3.1399158781,0.0814915536,-0.4349181022
C,0,1.4068611719,2.0213639832,2.6292617439
C,0,0.3103315345,2.9232782101,2.6928481259
C,0,2.6150029445,2.3603516,3.2968557405
C,0,0.4249176282,4.1119321589,3.3878957223
H,0,-0.6208157773,2.6787109419,2.198557377
C,0,2.7179504577,3.5513207443,3.989804217
H,0,3.4577982392,1.6821359212,3.2670747512
C,0,1.6262461183,4.4264738127,4.0342168977
H,0,-0.4121987666,4.7970745279,3.4364631834
H,0,3.6384549018,3.8067386031,4.4996868975
H,0,1.7108090565,5.3588993863,4.5808277288

*Structure 5*

Charge = 1 Multiplicity = 1
C,0,-0.4681975694,-0.4237712998,0.9222196372
C,0,0.3483338557,-0.5592194066,2.2065634043
C,0,1.6523728002,0.489786886,0.6559646721
C,0,0.3006460532,0.1940752183,0.0083112957
C,0,1.05827172,0.7617468538,2.0191518644
C,0,1.5055388682,-1.5807532789,1.9558591147
H,0,2.0553680204,-1.765442863,2.8807133512
H,0,1.1049905685,-2.5327520729,1.6076079173
C,0,2.3953819093,-0.8649249435,0.8971291136
H,0,3.402088373,-0.6833740316,1.2785020249
H,0,2.4855742365,-1.4217695318,-0.0355061949
H,0,-0.2244016777,-0.7158671171,3.1157873574
H,0,2.2422223286,1.2684439657,0.1812291589
H,0,-1.4807769482,-0.7855968005,0.8014449583
H,0,0.0463710097,0.4411921595,-1.0139900175
C,0,1.0781023272,1.9016928976,2.8114001902
C,0,1.803838622,3.0654984082,2.408161608
C,0,0.388595459,1.9479699898,4.0681405277
C,0,1.843835672,4.1929546283,3.1870822277
H,0,2.3383559263,3.0585638861,1.466965533
C,0,0.4215632878,3.0662443973,4.8494418251
H,0,-0.1671144419,1.0823419697,4.4043436844
C,0,1.1487789602,4.2094014776,4.422911832
H,0,2.4033582633,5.0573124238,2.858140176
H,0,-0.0934692854,3.1151264334,5.8003863861
O,0,1.1209869209,5.2370697512,5.2473252779
C,0,1.8190492514,6.4653330279,4.9409468884
H,0,1.6185111128,7.1198706113,5.7841288687
H,0,2.8913995845,6.2805425294,4.8583221012
H,0,1.42514412,6.9062355854,4.0236745508

*Structure 6*

Charge = 1 Multiplicity = 1
C,0,1.0610721071,0.4166069759,-0.071976316
C,0,0.1488701726,0.2534514927,1.1356193083
C,0,2.2730507655,-0.3527734566,1.7654327682
C,0,2.3163997216,0.0577782192,0.300173705
C,0,1.2859565585,0.7688900614,1.9848701264
C,0,0.0076491651,-1.2416671678,1.5312431605
H,0,-0.7004746818,-1.3423253366,2.3555015686
H,0,-0.3729491891,-1.8241052393,0.6922208822
C,0,1.4433950272,-1.6512798492,1.9575304936
H,0,1.4787005451,-1.9631023664,3.0027419294
H,0,1.8551404048,-2.4605427283,1.354545315
H,0,-0.7713000489,0.8272167832,1.0939911155
H,0,3.2285926039,-0.3134146136,2.2784750107

H,0,0.7586191022,0.8471945222,-1.0185404562
H,0,3.2213870448,0.1430767677,-0.2885224758
C,0,1.4388316402,2.0089212266,2.6660810182
C,0,0.3827852739,2.9522133366,2.6895404231
C,0,2.6288211867,2.2944352134,3.3805516305
C,0,0.5169506778,4.1375872838,3.3900270004
H,0,-0.54052027,2.7508246003,2.1623628589
C,0,2.756926903,3.4786766536,4.0818000455
H,0,3.4441291906,1.5831212776,3.3883810383
C,0,1.7023474675,4.3984712943,4.0838019972
H,0,-0.2927425395,4.8552003803,3.4126631315
H,0,3.6626535586,3.691248486,4.6353333675
C,0,1.8740565963,5.7157803359,4.821594728
F,0,2.5706392741,5.5475340155,5.9576899586
F,0,2.5487253611,6.5899834288,4.0493071265
F,0,0.6908155216,6.2662271991,5.1328156356

*Structure 7*

Charge = 1 Multiplicity = 1
C,0,-0.2249192587,0.2975928903,0.5782123199
C,0,0.3414220007,0.0177205026,2.0483829311
C,0,2.1345543001,-0.2252375254,0.6655477426
C,0,1.0227282807,0.1626657167,-0.3348958663
H,0,-1.0451777952,-0.3687560246,0.3103011172
H,0,-0.6197425008,1.3151360852,0.60256705
H,0,0.8898718222,-0.5846526351,-1.1190970286
H,0,1.2572075245,1.109839552,-0.8226845811
C,0,1.7694839774,0.6104205095,1.9050682163
H,0,2.4038203137,0.4158899468,2.7727336495
H,0,1.7399992368,1.6852626893,1.7214490737
C,0,0.5776616036,-1.4371021334,2.0112485242
C,0,1.8191434158,-1.6445902729,1.1922498563
H,0,2.616043121,-1.9686069683,1.8789713867
H,0,1.7199108525,-2.4234537973,0.4321599361
H,0,-0.3026587724,0.4023647165,2.833126295
H,0,3.1501217807,-0.1198738239,0.2896946661
C,0,-0.2231370518,-2.4537996284,2.5803831467
C,0,-1.3708282393,-2.1328377774,3.3596310874
C,0,0.1130063579,-3.8253298552,2.3972504388
C,0,-2.1398134055,-3.1340342891,3.9196185919
H,0,-1.6465068262,-1.0985982386,3.5171917646
C,0,-0.6594549384,-4.8187282087,2.9647772885
H,0,0.9834037029,-4.0944633054,1.8125990628
C,0,-1.7853629473,-4.4743736079,3.7238147984
H,0,-3.0119500919,-2.8851378531,4.5111633494
H,0,-0.3979959947,-5.8601998115,2.8252259023
H,0,-2.390097607,-5.2572397283,4.1677090894

*Structure 8*

Charge = 1 Multiplicity = 1
C,0,-0.3805903922,0.3313689786,0.8960151125
C,0,0.4554379578,-0.110628097,2.1686263362
C,0,1.96979546,-0.0785119151,0.4709411416
C,0,0.6751721948,0.3666038115,-0.2461103875
H,0,-1.2209848389,-0.3345606982,0.6968201233
H,0,-0.7874621891,1.3212153705,1.1118057117
H,0,0.4156689343,-0.2912460704,-1.0776642185
H,0,0.7845449942,1.3741175963,-0.6500314477
C,0,1.8151819593,0.5713345258,1.8590225491
H,0,2.6053701899,0.3001775178,2.5629245229
H,0,1.7235891559,1.658224494,1.8306363854
C,0,0.7521407888,-1.5442709697,1.9140388672
C,0,1.8181090051,-1.5701644592,0.8471133744
H,0,2.7494726298,-1.9410074172,1.2977277639
H,0,1.5794916582,-2.236093674,0.0134659094
H,0,-0.029837133,0.132409112,3.1098026472
H,0,2.889695666,0.1401080824,-0.0679419898
C,0,0.1491118776,-2.6590711763,2.4990443782
C,0,-0.8518513941,-2.5216382525,3.5100009921
C,0,0.5165166873,-3.9899525343,2.1110809341
C,0,-1.4482424892,-3.6125802096,4.0893312442
H,0,-1.1544166008,-1.5334614652,3.8310508062
C,0,-0.0669372927,-5.0827818855,2.683553924
H,0,1.2745128885,-4.1352875081,1.351883685
C,0,-1.0619966231,-4.9140613236,3.682940792
H,0,-2.2030978997,-3.4740229303,4.8504332974
H,0,0.2050415525,-6.0914542896,2.3996464742
O,0,-1.5658184455,-6.028978545,4.1735640743
C,0,-2.5858691248,-6.0050086214,5.1974427917
H,0,-3.4807795501,-5.5006953041,4.8289059249
H,0,-2.8045161683,-7.0493529131,5.4003442966
H,0,-2.2063610266,-5.5207823051,6.0988253199

*Structure 9*

Charge = 1 Multiplicity = 1
C,0,-0.2552729898,0.3030959104,0.6646177367
C,0,0.3950406053,0.0040445856,2.1044082294
C,0,2.0997791481,-0.2397397843,0.6130820368
C,0,0.9365051351,0.1713328419,-0.3177716972
H,0,-1.0960897081,-0.3523820613,0.437308011
H,0,-0.6388538748,1.3230993705,0.7315872092
H,0,0.753324476,-0.5631947176,-1.1036755164
H,0,1.1519628174,1.1237825971,-0.8040082106
C,0,1.8164312692,0.5847948521,1.8806857093
H,0,2.4989388753,0.3749675762,2.7072374316
H,0,1.7864061138,1.6616722746,1.7105208802

C,0,0.6024952324,-1.4488541446,2.0238575572
C,0,1.7942211118,-1.6616731465,1.1397463958
H,0,2.620428471,-1.9984466525,1.785828548
H,0,1.651410929,-2.4343985593,0.3804104681
H,0,-0.202568077,0.3869028414,2.9258210256
H,0,3.0935273389,-0.1432952248,0.1811391922
C,0,-0.1956673989,-2.4670875031,2.6091674896
C,0,-1.2876000513,-2.1415853541,3.4573808965
C,0,0.0941662822,-3.8376356088,2.3715102767
C,0,-2.0542880905,-3.1373520614,4.0318638799
H,0,-1.528019687,-1.107216013,3.6630689346
C,0,-0.6711849983,-4.830004859,2.951444797
H,0,0.9244332045,-4.115340136,1.7352914884
C,0,-1.744829702,-4.4781715501,3.7786693571
H,0,-2.882557017,-2.8861254915,4.6816082405
H,0,-0.4425273403,-5.8732615398,2.7755506646
C,0,-2.6165432993,-5.5746154133,4.3709813988
F,0,-1.9008078928,-6.6806664462,4.6259813068
F,0,-3.1976694221,-5.1771515505,5.5125789375
F,0,-3.5902212411,-5.9010274548,3.4992199503

*Cyclopentene*

Charge = 0 Multiplicity = 1
C,0,-0.9872655082,0.2142156248,-0.7106657544
C,0,-0.8606010785,0.487531982,0.8117462799
C,0,0.6086115947,0.2532872824,1.0808272007
C,0,1.2176628381,-0.3420404716,0.055276458
C,0,0.2682336702,-0.6158672192,-1.0890417527
H,0,-0.9679017242,1.164619311,-1.2508712578
H,0,-1.4725234275,-0.2060567315,1.4038871098
H,0,-1.1877535567,1.4960535101,1.0835890553
H,0,1.0830855487,0.5106190867,2.0212896963
H,0,2.2601668315,-0.6399395303,0.0392617525
H,0,0.0449894585,-1.689376153,-1.1513764809
H,0,0.6802874335,-0.3298957167,-2.061911172
H,0,-1.9201996615,-0.2887869667,-0.9727232927