

ACCESSORY PUBLICATION

New Thermal Routes to *ortho*-Benzyne

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Contents

Computational Methods	page S-1
References	page S-1
Table1. Energies of Stationary Points	page S-2
Computational Results for Stationary Points	pages S-3 to S-10

Computational Methods

All stationary points were optimized at the B3LYP/6-311+G(d,p) level of theory, followed by vibrational frequency analysis and CCSD(T) single point calculation with the same basis set. Spartan 08^[1] was used for initial calculations, followed by further optimization with Gaussian 03.^[2] Structures that were not obviously closed shell were subjected to a stability check on the wavefunction. All transition states as well as intermediate **27** were found to have significant open shell character. Energies are summarized in Table 1.

References

- [1] Spartan 08, Wavefunction Inc, Irvine, California., 2008.
- [2] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V.

Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Table 1. Energies of Stationary Points

	B3LYP/6-311+G**			CCSD(T)/6-311+G**//B3LYP	
	E+ZPE (hartree)	E rel (kcal/mol)	ZPE (hartree)	E+ZPE^a (hartree)	E rel (kcal/mol)
1	-230.897793		0.074892	-230.2536448	
1,3-butadiyne	-153.493378		0.037598	-153.0677235	
1 + 1,3-butadiyne	-384.391171	0.0			0.0
TS1	-384.38145	6.1	0.112044	-383.3042075	10.8
27	-384.431341	-25.2	0.114762	-383.3531197	-19.9
TS2	-384.428035	-23.1	0.115165	-383.3501493	-18.1
TS3	-384.41776	-16.7	0.116019	-383.3446928	-14.6
28	-384.491639	-63.0	0.118998	-383.4263125	-65.9
23	-384.526357	-84.8	0.121683	-383.4734962	-95.5

a) CCSD(T) energies corrected with B3LYP zero point energies.

B3LYP/6-311+G and CCSD(T)/6-311+G**//B3LYP/6-311+G**
Computational Results for Stationary points**

1 ortho-Benzynes

Charge = 0 Multiplicity = 1

C,0,0.0022994087,0.,0.0008006067
C,0,0.0050322854,0.,1.3832693924
C,0,0.9974043156,0.,2.1345244741
C,0,2.3287338942,0.,1.7619805638
C,0,2.444435667,0.,0.3559114185
C,0,1.3242028978,0.,-0.4921380377
H,0,-0.8619827702,0.,-0.6504229075
H,0,3.1900673004,0.,2.4170992659
H,0,3.4367386779,0.,-0.0837233311
H,0,1.4780480894,0.,-1.566510243

E(UB+HF-LYP) = -230.97268495 a.u.

Zero-point correction=	0.074892 (Hartree/Particle)
Thermal correction to Energy=	0.079363
Thermal correction to Enthalpy=	0.080307
Thermal correction to Gibbs Free Energy=	0.048196
Sum of electronic and zero-point Energies=	-230.897793
Sum of electronic and thermal Energies=	-230.893322
Sum of electronic and thermal Enthalpies=	-230.892378
Sum of electronic and thermal Free Energies=	-230.924489

HF=-229.4721957\MP2=-
230.1973826\MP3=-230.2352783\MP4D=-230.2526637\MP4DQ=-230.2344243\PUHF
=-229.6582633\PMP2-0=-230.3797768\PMP3-0=-230.4105037\MP4SDQ=-230.2496
565\CCSD=-230.2818605\CCSD(T)=-230.3285368\S2=1.320463\S2-1=1.137879\S
2A=3.427877\RMSD=1.039e-09\Thermal=0.\PG=C02V [SGV(C6H4)]\@\

1,3-butadiyne

Charge = 0 Multiplicity = 1

C,0,-0.4654363931,-0.54687499,0.
H,0,-1.5280913364,-0.54687499,0.
C,0,0.7418693089,-0.54687499,0.
C,0,2.1067807111,-0.54687499,0.
C,0,3.3140864131,-0.54687499,0.
H,0,4.3767413564,-0.54687499,0.

E(UB+HF-LYP) = -153.53097590 a.u.

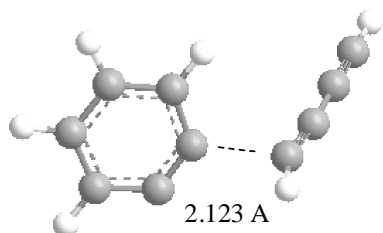
Zero-point correction=	0.037598 (Hartree/Particle)
Thermal correction to Energy=	0.041895
Thermal correction to Enthalpy=	0.042840
Thermal correction to Gibbs Free Energy=	0.014870
Sum of electronic and zero-point Energies=	-153.493378
Sum of electronic and thermal Energies=	-153.489080
Sum of electronic and thermal Enthalpies=	-153.488136

Sum of electronic and thermal Free Energies= -153.516106

HF=-152.5351098\MP2=-153.0621592\MP3=-153.0676488\MP4D=-153.0840089\MP4DQ=-153.068809\PUHF=-152.5351098\PMP2-0=-153.0621592\PMP3-0=-153.0676488\MP4SDQ=-153.0766534\CCSD=-153.0762359\CCSD(T)=-153.1053215\S2=0.\S2-1=0.\S2A=0.\RMSD=1.926e-09\Thermal=0.\PG=D*H [C*(H1C1C1.C1C1H1)]\@

vita

TS1 1 + butadiyne



Charge = 0 Multiplicity = 1

H,0,0.0038153414,0.1310909265,-0.0143818621
C,0,0.0081127435,0.0687846778,1.067060877
C,0,0.0614510243,-0.0916314148,3.941587702
C,0,1.1150221384,-0.2273112201,1.8464161255
C,0,-1.1409516966,0.3017148046,1.8397955066
C,0,-1.1158818518,0.2235695158,3.2407526803
C,0,1.1521580696,-0.3187349385,3.113781263
H,0,-2.0706924851,0.5470651,1.3371397271
H,0,-2.0312220503,0.40053495,3.797457657
H,0,0.0734545084,-0.159738913,5.023407022
C,0,2.8972907166,-0.3975094102,0.7060197132
H,0,3.345588598,0.5041593844,1.059127677
C,0,2.891289794,-1.4151595882,0.015032192
C,0,2.7173309261,-2.5746262392,-0.6601687851
C,0,2.5809360116,-3.6097892266,-1.2748979678
H,0,2.458271452,-4.5200769647,-1.8096007459

E(UB+HF-LYP) = -384.49349398 a.u.

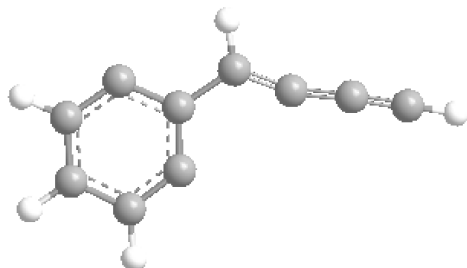
S2=0.084019

Imaginary Frequency = -673.182

Zero-point correction= 0.112044 (Hartree/Particle)
Thermal correction to Energy= 0.121475
Thermal correction to Enthalpy= 0.122419
Thermal correction to Gibbs Free Energy= 0.076054
Sum of electronic and zero-point Energies= -384.381450
Sum of electronic and thermal Energies= -384.372019
Sum of electronic and thermal Enthalpies= -384.371075
Sum of electronic and thermal Free Energies= -384.417440

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 49795\PMP3-0=-382.1539546\MP4SDQ=-383.2955028\CCSD=-383.3398268\CCSD(T
)=-383.4162515\S2=2.212207\S2-1=1.885921\S2A=8.598481\RMSD=6.692e-09\T
 hermal=0.\PG=C01 [X(C10H6)]\@

27 diradical intermediate



Charge = 0 Multiplicity = 1
 H,0,0.,0.,0.
 C,0,0.,0.,1.08580973
 C,0,0.0136415851,0.,3.8934287395
 C,0,-1.2326037816,0.0005320652,1.7709815556
 C,0,1.2060629883,-0.0005206086,1.7836938671
 C,0,1.2242919523,-0.0005284773,3.1781984977
 C,0,-1.1395452813,0.0004964595,3.1573015092
 H,0,2.1404268975,-0.0009239358,1.2342407835
 H,0,2.1669300587,-0.0009353761,3.7146433749
 H,0,0.006038076,0.0000067813,4.977910185
 C,0,-2.507907421,0.0010825622,1.0588183752
 H,0,-2.4504399307,0.0010577558,-0.0329813538
 C,0,-3.6987072654,0.0015965824,1.6293888654
 C,0,-4.9913774739,0.0019900893,1.8845216395
 C,0,-6.1861902397,0.0019044881,2.1876074254
 H,0,-7.2172964782,0.0021794978,2.4435120085

E(UB+HF-LYP) = -384.54610232

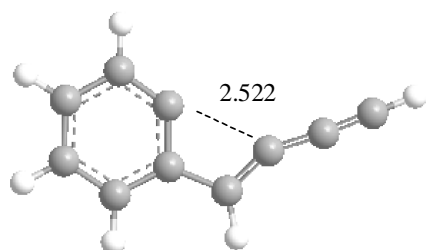
S2=1.037891

Zero-point correction=	0.114762 (Hartree/Particle)
Thermal correction to Energy=	0.123858
Thermal correction to Enthalpy=	0.124802
Thermal correction to Gibbs Free Energy=	0.079995
Sum of electronic and zero-point Energies=	-384.431341
Sum of electronic and thermal Energies=	-384.422244
Sum of electronic and thermal Enthalpies=	-384.421300
Sum of electronic and thermal Free Energies=	-384.466107

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 433299\MP4D=-383.3714321\MP4DQ=-383.3424003\PUHF=-381.6799793\PMP2-0=-

382.8584761\PMP3-0=-382.9172382\MP4SDQ=-383.3662369\CCSD=-383.3991833\
CCSD(T)=-383.4678818\S2=2.520759\S2-1=2.220397\S2A=9.2805\RMSD=8.973e-
09\Thermal=0.\PG=C01 [X(C10H6)]\@\@

TS2 closure to ethynylbenzocyclobutadiene



Charge = 0 Multiplicity = 1

H,0,0.0028860445,0.0000194504,0.001953288
C,0,-0.0001434836,0.0000089157,1.0870805198
C,0,0.009968806,-0.0000148358,3.9227851919
C,0,-1.2076517428,-0.0002649289,1.7936695568
C,0,1.2047926393,0.0002692528,1.7983242085
C,0,1.2177807926,0.0002593864,3.1916234154
C,0,-1.1421873761,-0.0002631937,3.1885722912
H,0,2.1438304549,0.0004821684,1.2567948933
H,0,2.1623128527,0.0004637433,3.7252307017
H,0,0.0157221487,-0.0000235332,5.0069654025
C,0,-2.5754708235,-0.0005635305,1.3123319343
H,0,-2.8390652059,-0.0006120345,0.2549608648
C,0,-3.4930338477,-0.0007759852,2.2761006989
C,0,-4.7475466532,-0.001060046,2.7381051453
C,0,-5.8579001138,-0.0013167285,3.2547263999
H,0,-6.8253647221,-0.0015390795,3.6940896581

E(UB+HF-LYP) = -384.54319982 a.u.

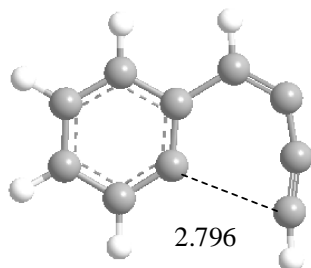
S2=0.755859

Imaginary Frequency = -224.947

Zero-point correction=	0.115165 (Hartree/Particle)
Thermal correction to Energy=	0.123305
Thermal correction to Enthalpy=	0.124249
Thermal correction to Gibbs Free Energy=	0.081910
Sum of electronic and zero-point Energies=	-384.428035
Sum of electronic and thermal Energies=	-384.419895
Sum of electronic and thermal Enthalpies=	-384.418951
Sum of electronic and thermal Free Energies=	-384.461290

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 383.3370444\PUHF=-381.6403502\PMP2-0=-382.8208683\PMP3-0=-382.8786891\
 MP4SDQ=-383.3612055\CCSD=-383.3954029\CCSD(T)=-383.4653143\S2=2.487882
 \S2-1=2.181927\S2A=9.211221\RMSD=0.000e+00\Thermal=0.\PG=C01 [X(C10H6)
]\@

TS3 closure to 2,3-naphthylene



Charge = 0 Multiplicity = 1
 H,0,0.00686603,0.,0.0028747724
 C,0,0.0056699385,0.,1.0873352486
 C,0,0.03267907,0.,3.8866506709
 C,0,1.167033927,0.,1.8176194138
 C,0,-1.2012199087,0.,1.8030446564
 C,0,-1.1762785153,0.,3.1984605427
 C,0,1.2665920971,0.,3.1977013128
 H,0,-2.1459405546,0.,1.2699978165
 H,0,-2.106681778,0.,3.7546815814
 H,0,0.0413144419,0.,4.972872635
 C,0,3.7673354949,0.,0.7889568984
 C,0,2.5326903868,0.,3.971383953
 H,0,2.4451855006,0.,5.053336922
 C,0,3.9182901603,0.,2.0079130764
 C,0,3.6952124496,0.,3.3265140788
 H,0,3.8041919204,0.,-0.2741508761

E(UB+HF-LYP) = -384.53377961 a.u.

S2=0.79588

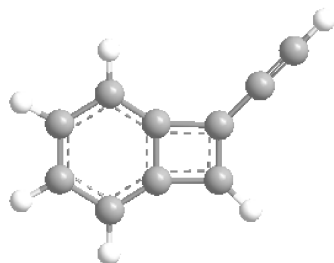
Imaginary Frequency = -196.597

Zero-point correction=	0.116019 (Hartree/Particle)
Thermal correction to Energy=	0.123720
Thermal correction to Enthalpy=	0.124664
Thermal correction to Gibbs Free Energy=	0.083621
Sum of electronic and zero-point Energies=	-384.417760
Sum of electronic and thermal Energies=	-384.410059
Sum of electronic and thermal Enthalpies=	-384.409115
Sum of electronic and thermal Free Energies=	-384.450159

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 MP4DQ=-383.329317\PUHF=-381.6358148\PMP2-0=-382.8228949\PMP3-0=

-382.8792694\MP4SDQ=-383.3540473\CCSD=-383.3894961\C
CSD(T)=-383.4607118\S2=2.482459\S2-1=2.183249\S2A=9.229774\RMSD=0.000e
+00\Thermal=0.\PG=CS [SG(C10H6)]\@

28 ethynylbenzocyclobutadiene



Charge = 0 Multiplicity = 1

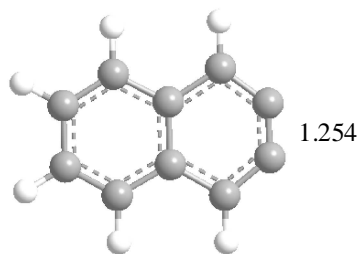
H,0,2.1361735824,-0.0077820728,-2.3986315843
C,0,1.785704108,-0.0036715648,-1.3731415373
C,0,0.9038395346,0.0075423119,1.3776511683
C,0,0.4679913973,-0.0039954755,-1.0249554026
C,0,2.7149760001,0.0023761412,-0.2834970196
C,0,2.2952229445,0.0076436434,1.0294002783
C,0,0.0413970638,0.0015842324,0.3282017003
H,0,3.776971765,0.0027970088,-0.5013506394
H,0,3.0331734888,0.012176633,1.8235705339
H,0,0.5896611957,0.0118816747,2.4145801885
C,0,-0.9778546352,-0.0079665342,-1.4631619625
H,0,-1.4898669994,-0.0129945933,-2.4153067547
C,0,-1.4131387629,-0.0027713935,-0.1722141538
C,0,-2.6622959992,-0.0015786288,0.4608747786
C,0,-3.7208168317,-0.0002968306,1.0425635256
H,0,-4.6562619473,0.000725941,1.5468100043

E(UB+HF-LYP) = -384.61063761 a.u.

Zero-point correction=	0.118998 (Hartree/Particle)
Thermal correction to Energy=	0.126843
Thermal correction to Enthalpy=	0.127788
Thermal correction to Gibbs Free Energy=	0.086459
Sum of electronic and zero-point Energies=	-384.491639
Sum of electronic and thermal Energies=	-384.483794
Sum of electronic and thermal Enthalpies=	-384.482850
Sum of electronic and thermal Free Energies=	-384.524179

HF=-382.1227758\
MP2=-383.3686376\MP3=-383.4218842\MP4D=-383.4522915\MP4DQ=-383.4203444
\PUHF=-382.3983732\PMP2-0=-383.6394784\PMP3-0=-383.6838288\MP4SDQ=-383
.4432395\CCSD=-383.4721983\CCSD(T)=-383.5453105\S2=1.437236\S2-1=1.212
823\S2A=4.372923\RMSD=2.920e-09\Thermal=0.\PG=C01 [X(C10H6)]\@

23 2,3-naphthylene



Charge = 0 Multiplicity = 1

C,0,-1.7753085186,0.,-1.6338746366
 C,0,-1.775194739,0.,-0.2608000788
 C,0,-0.5591435336,0.,0.4762605834
 C,0,0.6891657543,0.,-0.2540003891
 C,0,0.6426214101,0.,-1.6752226019
 C,0,-0.5542140188,0.,-2.3482149573
 H,0,-1.5083601704,0.,2.4681437408
 H,0,-2.7143813512,0.,-2.1755874423
 H,0,-2.7121294547,0.,0.2860468088
 C,0,-0.5762303528,0.,1.9169796161
 C,0,1.9533953685,0.,0.4371484897
 H,0,1.5784578434,0.,-2.2239468952
 H,0,-0.5662130638,0.,-3.4322659579
 C,0,1.7711136134,0.,1.786287378
 C,0,0.6891259863,0.,2.4192501738
 H,0,2.8906403779,0.,-0.105271718

E(UB+HF-LYP) = -384.64803926 a.u.

Zero-point correction=	0.121683 (Hartree/Particle)
Thermal correction to Energy=	0.128596
Thermal correction to Enthalpy=	0.129540
Thermal correction to Gibbs Free Energy=	0.091190
Sum of electronic and zero-point Energies=	-384.526357
Sum of electronic and thermal Energies=	-384.519443
Sum of electronic and thermal Enthalpies=	-384.518499
Sum of electronic and thermal Free Energies=	-384.556849

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 3.4902161\PMP3-0=-383.5040303\MP4SDQ=-383.5129859\CCSD=-383.5139002\CC
 SD(T)=-383.5951792\S2=0.\S2-1=0.\S2A=0.\RMSD=3.509e-09\Thermal=0.\PG=C
 02V [SGV(C10H6)]\@