Published in "Physical Chemistry Chemical Physics 17(16): 10624–10629, 2015"
which should be cited to refer to this work.

Supporting Information

Electromers of the Benzene Dimer Radical Cation

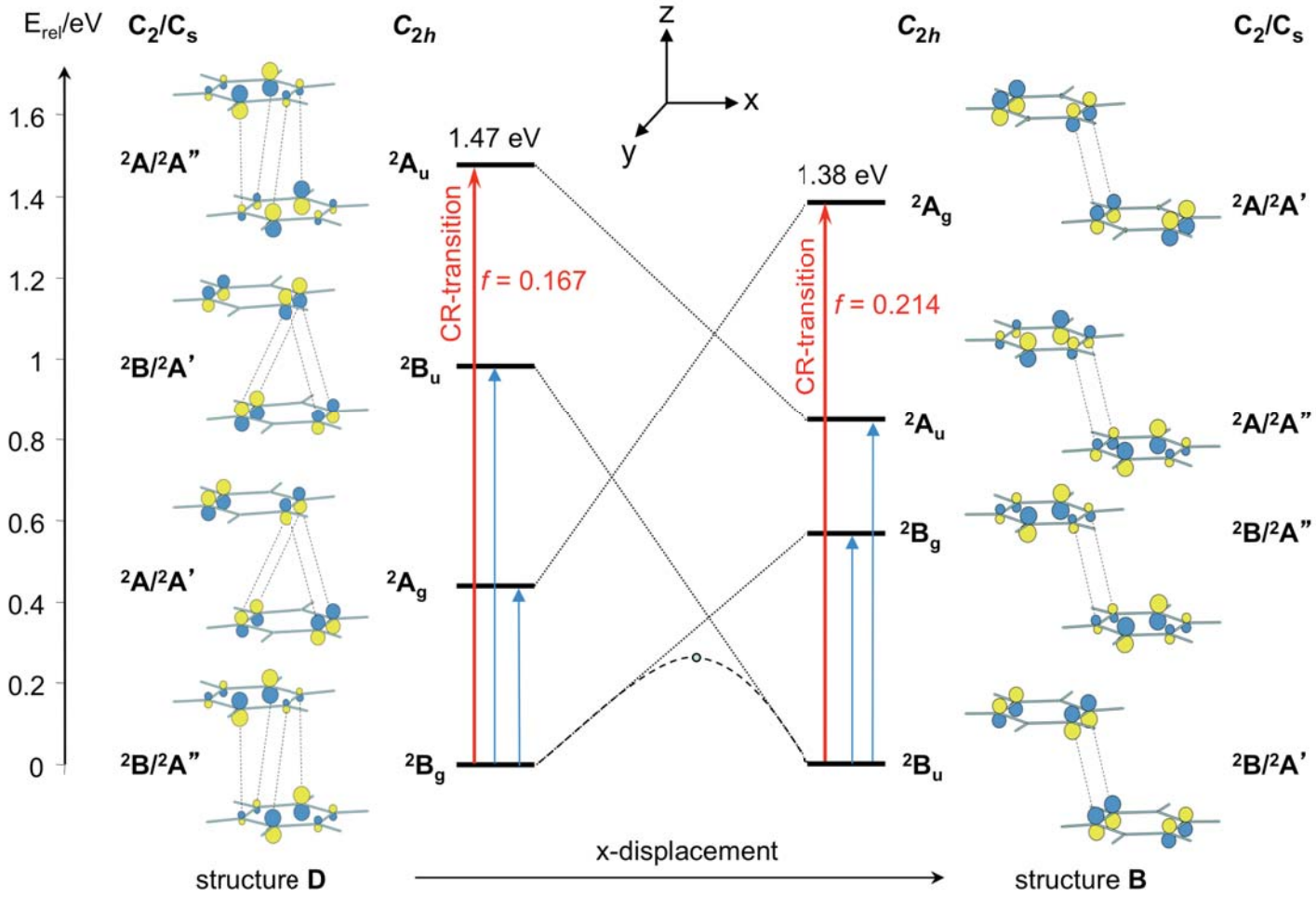
Anna Błoch-Mechkour and Thomas Bally*

Department of Chemistry, University of Fribourg, Switzerland

Full citation of the Gaussian program (Ref 25):

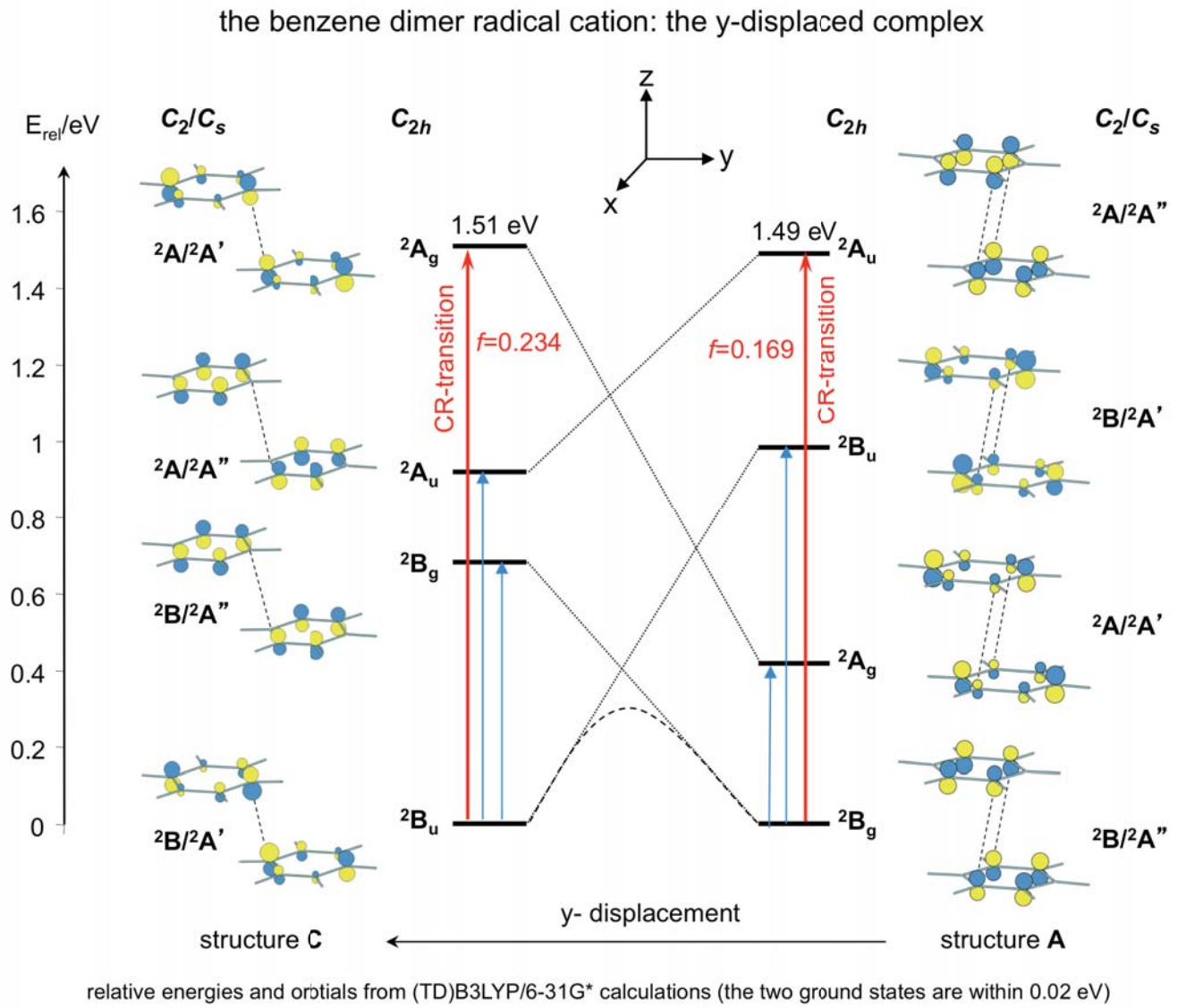
Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

the benzene dimer radical cation: the x-displaced complex



relative energies and orbtials from (TD)B3LYP/6-31G* calculations (the two ground states are within 0.02 eV)

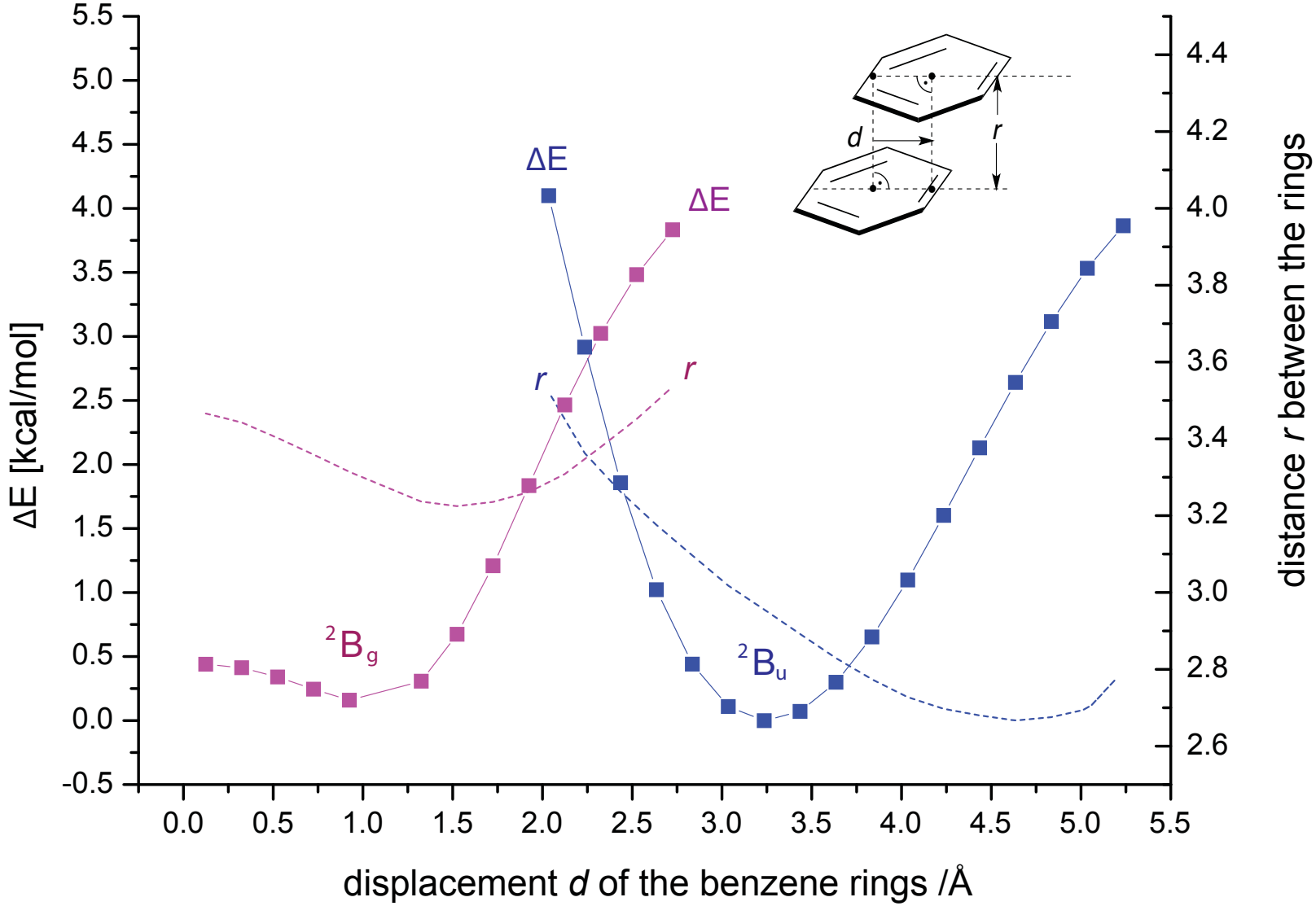
Note: On passing from the ^2B_u to the ^2B_g ground state of the two x-displaced structures, the system encounters a conical intersecton, below which lies a transition state which can only be attained by localizing the spin and chrarge on one of the two benzene rings. Unfortunately such transition states are unattainable by DFT calculations, because the self-repulsion error prevents localization of spin and charge in such systems



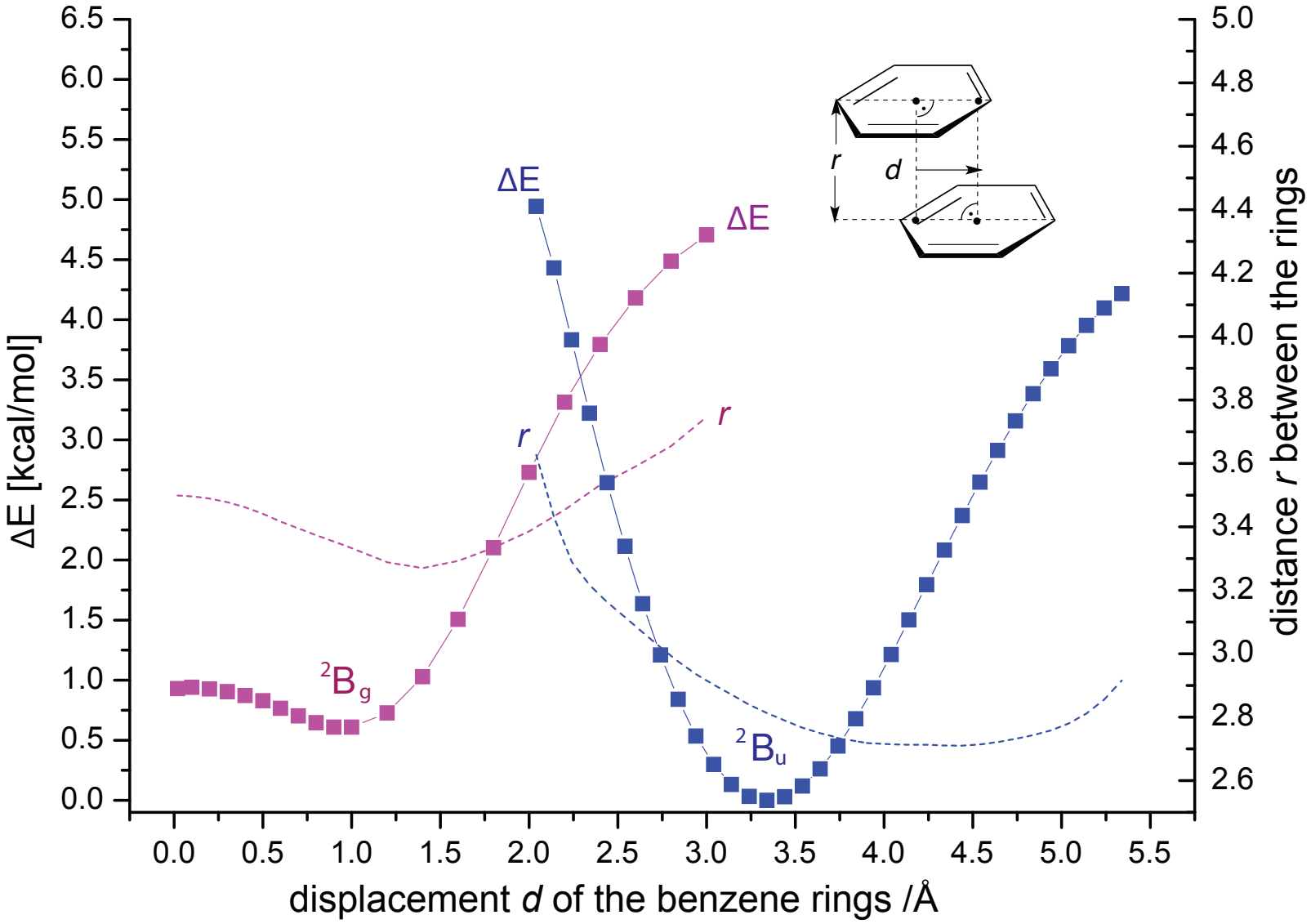
relative energies and orbitals from (TD)B3LYP/6-31G* calculations (the two ground states are within 0.02 eV)

Note: On passing from the ^2B_u to the ^2B_g ground state of the two y-displaced structures, the system encounters a conical intersecton, below which lies a transition state which can only be attained by localizing the spin and chrarge on one of the two benzene rings. Unfortunately such transition states are unattainable by DFT calculations, because the self-repulsion error prevents localization of spin and charge in such systems

The benzene dimer cation: potential surfaces for x-displacement (from UB3LYP/6-31G* calculations)



The benzene dimer cation: potential surfaces for x-displacement (from UB3LYP/6-31G* calculations)



All stationary points listed below were located and characterized by **B2-PLYP-D/cc-pVDZ.**

structure A (2Bg, y-displaced, “half shift”):

6	1.501529	1.253419	1.204442
6	1.501529	1.253419	-1.204442
6	-1.501529	-1.253419	-1.204442
6	-1.501529	-1.253419	1.204442
6	1.501529	-0.175104	-1.205612
6	1.501529	-0.175104	1.205612
6	-1.501529	0.175104	1.205612
6	-1.501529	0.175104	-1.205612
6	1.518867	1.961582	0.000000
6	-1.518867	-1.961582	0.000000
6	1.534199	-0.880091	0.000000
6	-1.534199	0.880091	0.000000
1	1.510909	1.788467	2.156627
1	1.510909	1.788467	-2.156627
1	-1.510909	-1.788467	-2.156627
1	-1.510909	-1.788467	2.156627
1	1.535585	-0.708412	2.157893
1	1.535585	-0.708412	-2.157893
1	-1.535585	0.708412	2.157893
1	-1.535585	0.708412	-2.157893
1	1.568617	-1.969805	0.000000
1	-1.568617	1.969805	0.000000
1	1.540097	3.052155	0.000000
1	-1.540097	-3.052155	0.000000

E(UB2PLYP-D/cc-pvDZ): -463.7208263 h
lowest frequency (bg): -13.0950 cm-1
E(G4): -463.870804 h
E(OO-SCS-RI-MP2/cc-pVTZ): -463.338667 h

structure B (2Bu, x-displaced, “full shift”)

6	0.002481	2.032686	1.420914
6	-0.002481	-2.032686	1.420914
6	0.002481	2.032686	-1.420914
6	-0.002481	-2.032686	-1.420914
6	0.826739	2.905238	0.711480
6	-0.826739	-2.905238	0.711480
6	0.826739	2.905238	-0.711480
6	-0.826739	-2.905238	-0.711480
6	-0.826739	1.145722	0.716123
6	0.826739	-1.145722	0.716123
6	-0.826739	1.145722	-0.716123
6	0.826739	-1.145722	-0.716123
1	-0.010289	2.046549	2.511831
1	0.010289	-2.046549	2.511831
1	-0.010289	2.046549	-2.511831
1	0.010289	-2.046549	-2.511831
1	1.470005	3.607223	1.245886
1	-1.470005	-3.607223	1.245886
1	1.470005	3.607223	-1.245886
1	-1.470005	-3.607223	-1.245886
1	-1.516780	0.489963	1.248730
1	1.516780	-0.489963	1.248730
1	-1.516780	0.489963	-1.248730
1	1.516780	-0.489963	-1.248730

E(UB2PLYP-D/cc-pVDZ): -463.715989 h
lowest frequency (bg): -37.6929 cm-1
(note: this structure has a second imaginary mode of au-symmetry at -9.34 cm-1)
E(G4): -463.864583 h
E(OO-SCS-RI-MP2/cc-pvTZ): -463.331188 h

structure C (2Bu, y-displaced, “full shift”)

6	1.347182	2.220114	1.229686
6	1.347182	2.220114	-1.229686
6	-1.347182	-2.220114	-1.229686
6	-1.347182	-2.220114	1.229686
6	1.347182	0.831576	1.234139
6	1.347182	0.831576	-1.234139
6	-1.347182	-0.831576	-1.234139
6	-1.347182	-0.831576	1.234139
6	1.343688	2.914523	0.000000
6	-1.343688	-2.914523	0.000000
6	1.329060	0.122406	0.000000
6	-1.329060	-0.122406	0.000000
1	1.372589	0.275611	2.172742
1	1.372589	0.275611	-2.172742
1	-1.372589	-0.275611	-2.172742
1	-1.372589	-0.275611	2.172742
1	1.364384	2.777486	2.167502
1	1.364384	2.777486	-2.167502
1	-1.364384	-2.777486	2.167502
1	-1.364384	-2.777486	-2.167502
1	1.352654	4.006791	0.000000
1	-1.352654	-4.006791	0.000000
1	1.380558	-0.967902	0.000000
1	-1.380558	0.967902	0.000000

E(UB2PLYP-D/cc-pVDZ): -463.717246 h
lowest frequency (au): 25.8259 cm-1
E(G4): -463.863734 h
E(OO-SCS-RI-MP2/cc-pVTZ): -463.333692 h

structure D (2Bg, x-displaced, “half shift”)

6	0.004479	1.590102	1.393307
6	-0.004479	-1.590102	1.393307
6	0.004479	1.590102	-1.393307
6	-0.004479	-1.590102	-1.393307
6	1.161486	2.025138	0.692992
6	-1.161486	-2.025138	0.692992
6	1.161486	2.025138	-0.692992
6	-1.161486	-2.025138	-0.692992
6	-1.161486	1.198031	0.695030
6	1.161486	-1.198031	0.695030
6	-1.161486	1.198031	-0.695030
6	1.161486	-1.198031	-0.695030
1	0.000428	1.603775	2.485837
1	-0.000428	-1.603775	2.485837
1	0.000428	1.603775	-2.485837
1	-0.000428	-1.603775	-2.485837
1	2.038171	2.358855	1.250683
1	-2.038171	-2.358855	1.250683
1	2.038171	2.358855	-1.250683
1	-2.038171	-2.358855	-1.250683
1	-2.056555	0.917010	1.251775
1	2.056555	-0.917010	1.251775
1	-2.056555	0.917010	-1.251775
1	2.056555	-0.917010	-1.251775

E(UB2PLYP-D/cc-pVDZ): -463.7209038 h
lowest frequency (au): 15.8094 cm-1
E(G4): -463.869385 h
E(OO-SCS-RI-MP2/cc-pVTZ): -463.338337 h

All stationary points listed below were located and characterized by **wB97X-D.**

structure A (2Bg, y-displaced, “half shift”):
symmetry: C2h

6	1.533876	1.215518	1.198654
6	1.533876	1.215518	-1.198654
6	-1.533876	-1.215518	-1.198654
6	-1.533876	-1.215518	1.198654
6	1.533876	-0.207914	-1.199270
6	1.533876	-0.207914	1.199270
6	-1.533876	0.207914	1.199270
6	-1.533876	0.207914	-1.199270
6	1.554056	1.920952	0.000000
6	-1.554056	-1.920952	0.000000
6	1.568234	-0.909917	0.000000
6	-1.568234	0.909917	0.000000
1	1.543589	1.748791	2.150958
1	1.543589	1.748791	-2.150958
1	-1.543589	-1.748791	-2.150958
1	-1.543589	-1.748791	2.150958
1	1.567596	-0.740247	2.151382
1	1.567596	-0.740247	-2.151382
1	-1.567596	0.740247	2.151382
1	-1.567596	0.740247	-2.151382
1	1.604363	-1.999244	0.000000
1	-1.604363	1.999244	0.000000
1	1.578861	3.010768	0.000000

E(wB97X-D/cc-pVDZ): -464.0632049 h
lowest frequency (bg): -24.8118 cm-1
E(OO-SCS-RI-MP2/cc-pVTZ): -463.339037 h

structure B (2Bu, x-displaced, “full shift”)
symmetry: C2h

6	0.001876	2.016596	1.415294
6	-0.001876	-2.016596	1.415294
6	0.001876	2.016596	-1.415294
6	-0.001876	-2.016596	-1.415294
6	0.839057	2.865272	0.708407
6	-0.839057	-2.865272	0.708407
6	0.839057	2.865272	-0.708407
6	-0.839057	-2.865272	-0.708407
6	-0.839057	1.145754	0.713390
6	0.839057	-1.145754	0.713390
6	-0.839057	1.145754	-0.713390
6	0.839057	-1.145754	-0.713390
1	-0.012919	2.032814	2.505424
1	0.012919	-2.032814	2.505424
1	-0.012919	2.032814	-2.505424
1	0.012919	-2.032814	-2.505424
1	1.495792	3.554110	1.242044
1	-1.495792	-3.554110	1.242044
1	1.495792	3.554110	-1.242044
1	-1.495792	-3.554110	-1.242044
1	-1.543362	0.506201	1.246033
1	1.543362	-0.506201	1.246033
1	-1.543362	0.506201	-1.246033
1	1.543362	-0.506201	-1.246033

E(wB97X-D/cc-pVDZ): -464.0575046 h

note: by this method this structure has three imaginary modes,two of au (-47.4 and -15.7 cm-1) one of bg symmetry (-49.2 cm-1)

E(OO-SCS-RI-MP2/cc-pVTZ): -463.332220 h

structure C (2B, y-displaced, “full shift”)
symmetry: C2, close to C2h

6	-0.000120	2.584974	-1.224567
6	0.000120	2.585113	1.224447
6	-0.000120	-2.585113	1.224447
6	0.000120	-2.584974	-1.224567
6	-0.722552	1.406835	-1.229786
6	-0.722379	1.406987	1.229911
6	0.722379	-1.406987	1.229911
6	0.722552	-1.406835	-1.229786
6	0.366436	3.170710	-0.000117
6	-0.366436	-3.170710	-0.000117
6	-1.069810	0.789218	0.000114
6	1.069810	-0.789218	0.000114
1	-1.039811	0.949126	-2.167472
1	-1.039595	0.949509	2.167727
1	1.039595	-0.949509	2.167727
1	1.039811	-0.949126	-2.167472
1	0.272401	3.071037	-2.161792
1	0.272840	3.071274	2.161548
1	-0.272401	-3.071037	-2.161792
1	-0.272840	-3.071274	2.161548
1	0.929036	4.106227	-0.000275
1	-0.929036	-4.106227	-0.000275
1	-1.695756	-0.104722	0.000248
1	1.695756	0.104722	0.000248

E(wB97X-D/cc-pVDZ): -464.0593409 h
lowest frequency (au): 24.9833 cm-1
E(OO-SCS-RI-MP2/cc-pVTZ): -463.334736 h

structure D (2B, x-displaced, “half shift”)
(transition state, C2, close to C2h structure)

6	-2.087896	-0.998594	0.487058
6	1.055497	-0.926031	1.269324
6	-1.083684	1.002767	-1.198147
6	2.120285	0.921624	-0.556525
6	-2.292010	0.325267	0.826107
6	1.724959	-1.357531	0.099108
6	-1.770164	1.331283	-0.001537
6	2.279250	-0.427188	-0.799377
6	-1.376041	-1.328766	-0.699787
6	0.920269	0.426944	1.525385
6	-0.908631	-0.324877	-1.552588
6	1.418615	1.354791	0.601275
1	-2.480855	-1.799239	1.115409
1	0.682540	-1.666236	1.978434
1	-0.736141	1.802561	-1.853498
1	2.536933	1.663119	-1.239723
1	-2.846837	0.590755	1.726244
1	1.848073	-2.426765	-0.084246
1	-1.925311	2.381084	0.254945
1	2.824659	-0.775509	-1.676777
1	-1.250731	-2.378349	-0.972160
1	0.427757	0.773947	2.433889
1	-0.404283	-0.587778	-2.482288
1	1.321507	2.424277	0.797990

E(wB97X-D/cc-pVDZ/cc-pVDZ): -464.0633024 h
lowest frequency (au): -23.0968 cm-1
E(OO-SCS-RI-MP2/cc-pVTZ): -463.3389326 h

```
---------------------------------------------
structure D (2Bg, x-displaced, “half shift”)
(minimum halfway between D and A, symmetry: C2)
---------------------------------------------
6        0.586690    1.404134   -1.350961
6       -0.586690   -1.404134   -1.350961
6        0.052574    1.750944    1.351004
6       -0.052574   -1.750944    1.351004
6       -0.586690    2.094616   -0.940066
6        0.586690   -2.094616   -0.940066
6       -0.844521    2.275032    0.403788
6        0.844521   -2.275032    0.403788
6        1.508837    0.936678   -0.405727
6       -1.508837   -0.936678   -0.405727
6        1.236395    1.090203    0.942213
6       -1.236395   -1.090203    0.942213
1        0.797001    1.295823   -2.416695
1       -0.797001   -1.295823   -2.416695
1       -0.142566    1.889005    2.416351
1        0.142566   -1.889005    2.416351
1       -1.270408    2.485697   -1.694980
1        1.270408   -2.485697   -1.694980
1       -1.734617    2.811172    0.733813
1        1.734617   -2.811172    0.733813
1        2.427889    0.452035   -0.735360
1       -2.427889   -0.452035   -0.735360
1        1.944251    0.741591    1.695363
1       -1.944251   -0.741591    1.695363
---------------------------------------------

E(wB97X-D/cc-pVDZ):          -464.0633024 h
lowest frequency (au):         13.8877 cm-1
E(OO-SCS-RI-MP2/cc-pVTZ):    -463.338932 h
```