

Supplementary Information

Spurious Phosphorus Pyramidalization Induced by Some DFT Functionals

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BP-Benzene

Initial geometries:

Table S1. Flat optimized geometry obtained from CC2/TZVPP (E = -1100.5933521590 a.u.)

Element	X / a.u.	Y / a.u.	Z / a.u.
B	3.55089871941596	-0.00000011262447	0.00000380089889
B	-1.77544532575721	3.07515738087760	-0.00000039543713
B	-1.77544549160926	-3.07515720306579	-0.00000038661777
P	-3.35919711388557	0.00000039274867	-0.00009777793732
P	1.67959457403245	2.90914197572068	-0.00011275129372
P	1.67959525994135	-2.90914200748911	-0.00011236665569
H	5.78978048768223	0.00000062111950	0.00005134648100
H	-5.99661826332810	-0.00000123829510	0.00006430647401
H	2.99829119353363	5.19322524278373	0.00006062864871
H	-2.89487213770026	5.01409222594405	0.00004159421129
H	-2.89487272018825	-5.01409120229556	0.00004143384229
H	2.99829081786306	-5.19322607542423	0.00006056738502

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Table S2. Distorted optimized geometry obtained from B3-LYP/TZVPP (E = -1102.10530927366 a.u.)

Element	X / a.u.	Y / a.u.	Z / a.u.
B	-2.54543921117353	-2.87962986623640	0.09750042567139
B	-1.88849960632745	3.08405954563806	1.16424386751151
B	3.02725508209623	-0.48318677647915	0.67149404600692
P	0.91600810867128	-3.11705119200983	-0.17550177298712
P	-3.84707453973651	0.34126440679499	0.29808651248260
P	1.55238758177308	2.66361436365985	0.85531122732440
H	-2.79292982646519	5.06135466415463	1.69252506607047
H	5.23690218061020	-0.76406892467767	0.88547359026130
H	-3.86757272144949	-4.67865680253514	-0.05052638178903
H	3.05304851994318	4.58891143666515	1.88322085877581
H	1.93570849526203	-5.54842236961564	0.07806716905773
H	-6.42251629580893	0.51817270035863	0.89014496368941

Table S3. Final total energy determined when starting from a flat initial geometry

Functional	Energy / a.u.
1	B3LYP -1102.10531
2	B97D -1102.22803
3	BHLYP -1102.23231
4	BP96 -1102.41449
5	PBE -1101.68587
6	PBE0 -1101.79363
7	PWLDA -1097.63969
8	Slater -1092.94458
9	TPSS -1102.39278
10	M05 -1102.22225
11	M06 -1102.17526
12	M062X -1102.18613
13	M08HX -1102.23040
14	M11 -1102.16683
15	wB97 -1102.23602
16	wB97X-D -1102.25414

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Initial geometries:

Table S4. Flat optimized geometry obtained from CC2/TZVPP ($E = -4395.4907665222$ a.u.)

Element	X / a.u.	Y / a.u.	Z / a.u.
B	-1.76706055639621	3.05083105330588	0.01287073664544
B	3.48595412636957	6.05710393953353	-0.00124991167056
B	-1.80613748063012	9.13974328034271	-0.00491533692784
B	-1.75856691661923	-3.05573485851752	0.01287073664544
B	3.52562747301536	0.00490380521166	0.01287073664544
B	-6.98858294818362	-0.00962713990351	-0.00124991167056
B	3.50262882181403	-6.04747679963006	-0.00124991167056
B	-7.01218112452985	-6.13403258112431	-0.00491533692784
B	8.81831860515999	-3.00571069921846	-0.00491533692784
B	-1.78200896028941	-9.14412129464827	-0.00548161817895
B	-7.02803685630693	6.11532567670628	-0.00548161817895
B	8.81004581659635	3.02879561794204	-0.00548161817895
P	1.73936448697168	3.02238779113406	0.01562015285067
P	-3.51930003981649	6.07734915894215	0.00547226560198
P	1.62244522631833	8.99440366680656	-0.00920908329138
P	-3.48714685069585	-0.00486006340912	0.01562015285067
P	1.74778236372425	-3.01752772772501	0.01562015285067
P	-3.50348873940371	-6.08647781749180	0.00547226560198
P	7.02278877922015	0.00912865854956	0.00547226560198
P	-8.60060468050559	-3.09212305116282	-0.00920908329138
P	6.97815945418723	-5.90228061564376	-0.00920908329138
P	1.64629174522308	-8.98945533943545	-0.00486959104825
P	-8.60824256274828	3.06899719631396	-0.00486959104825
P	6.96195081752522	5.92045814312150	-0.00486959104825
H	2.99505329914733	11.25258211608438	-0.02285907444744
H	-2.91636085437588	11.08681031351687	-0.01085302630038
H	-11.24254862027315	-3.03249881529219	-0.02285907444744
H	8.24749532112589	-8.22008330079218	-0.02285907444744
H	3.02454789009356	-11.24414221858359	-0.02442653510919
H	-11.24998675010534	3.00273580150818	-0.02442653510919
H	8.22543886001179	8.24140641707545	-0.02442653510919
H	-8.14327895125698	-8.06904774325044	-0.01085302630038
H	11.05963980563283	-3.01776257026643	-0.01085302630038
H	-2.88728314352047	-11.09405440042646	-0.01224266535808
H	-8.16409136997561	8.04748775042058	-0.01224266535808
H	11.05137451349609	3.04656665000592	-0.01224266535808

Table S5. Distorted optimized geometry obtained from B3-LYP/TZVPP (E = -4401.40782253183 a.u.)

Element	X / a.u.	Y / a.u.	Z / a.u.
B	-1.77747798814734	3.03455717352638	-0.02349141325742
B	3.50083899394687	6.07839844042031	-0.00472614411283
B	-1.75839589980206	9.10265737334531	-0.11466309484855
B	-1.77015905235819	-3.07388988707489	-0.00833574109758
B	3.51526337561018	-0.01358783015464	-0.01260587700170
B	-7.04518568975161	-0.02699770627219	-0.02775467767816
B	3.51452832766462	-6.10609335880169	-0.00348425023371
B	-7.03530398814953	-6.09219658449640	-0.07757863843140
B	8.76077710541781	-3.06374332778843	-0.10343989727929
B	-1.73723866324937	-9.14147461684840	0.10851485183076
B	-7.04980512676083	6.04089860294532	0.04196889137090
B	8.75390682153661	3.04810204837388	0.08417430035031
P	1.74130013867024	3.02536363041847	-0.01337090855031
P	-3.54343089345321	6.08486625576861	-0.03275873623095
P	1.68231971184860	9.02513534067753	-0.63001543109672
P	-3.52158571776634	-0.02177132863488	-0.02281251770426
P	1.74844478023499	-3.05666280807832	-0.01030714091637
P	-3.52914660486583	-6.12839493724349	0.00691000932417
P	7.03977637334763	-0.00964670487930	-0.01390103640664
P	-8.68819528667652	-3.07995589174372	-0.63469878424381
P	6.97509967796239	-6.00376407634173	-0.63491348345016
P	1.70199480536640	-9.05407705455922	0.63486206836428
P	-8.69601483056793	3.02157024344767	0.57304390593031
P	6.96150924593508	5.98158252724546	0.62863083669103
H	2.94631166486070	11.23108005813982	0.13153726886215
H	-2.85040207096394	11.05444884695082	-0.02213271444857
H	-11.22897930331157	-3.07921021848932	0.13409692167128
H	8.25246950144526	-8.20160307480246	0.12850483563540
H	2.97186367604360	-11.25998308464903	-0.11724947307385
H	-11.23846176977178	3.01693286895664	-0.18940906327958
H	8.23350465070670	8.18552952872314	-0.12614270762660
H	-8.18038619624858	-8.01188075318801	0.03785319551453
H	10.99685963566452	-3.09397161740055	-0.00696657125846
H	-2.82445069295472	-11.09621731569329	0.02135003934676
H	-8.19902684485693	7.95852731456482	-0.06487452812270
H	10.98984332412456	3.08362644261077	-0.01391069920471

Table S6. Final total energy determined when starting from a flat initial geometry for different basis sets

Functional		Final total energy / a.u.		
		SVP	TZVPP	QZVPP
1	B3LYP	-4399.72335	-4401.40525	-4401.58976
2	B97D	-4400.17966	-4401.84785	-4402.02104
3	BHLYP	-4400.25483	-4401.92120	-4402.08592
4	BP96	-4400.96262	-4402.64224	-4402.82893
5	PBE	-4398.13089	-4399.80328	-4399.98882
6	PBE0	-4398.55826	-4400.21231	-4400.38014
7	PWLDA	-4382.10185	-4383.80135	-4384.03400
8	Slater	-4363.87389	-4365.56899	-4365.80130
9	TPSS	-4400.88490	-4402.53358	-4402.69925
10	M05	-4400.33954	-4401.91873	-4402.10886
11	M06	-4400.07260	-4401.70126	-
12	M062X	-4400.15652	-4401.78508	-4401.97286
13	M08HX	-4400.21032	-4401.91585	-
14	M11	-4399.89942	-4401.69029	-
15	wB97	-4400.31379	-4401.95327	-
16	wB97X-D	-4400.34762	-4402.00273	-

Table S7. Torsion angles and energy differences between the flat and distorted structures obtained from several XC functionals with a QZVPP basis

Functional		ΔE / eV	Torsion angle ^a / degree	Torsion angle ^b / degree
1	B3LYP	6.6×10^{-2}	0.03	20.27
2	B97D	6.6×10^{-2}	0.03	19.74
3	BHLYP	1.5×10^{-1}	0.03	23.61
4	BP96	9.5×10^{-3}	0.03	13.27
5	PBE	1.6×10^{-3}	0.03	7.89
6	PBE0	1.1×10^{-2}	0.03	14.20
7	PWLDA	0.0	0.04	0.08
8	Slater	0.0	0.03	0.30
9	TPSS	8.7×10^{-3}	0.03	10.90
10	M05	1.8×10^{-1}	0.95	25.64
12	M062X	7.2×10^{-3}	2.19	11.72

^aFlat initial geometry; ^bdistorted initial geometry.

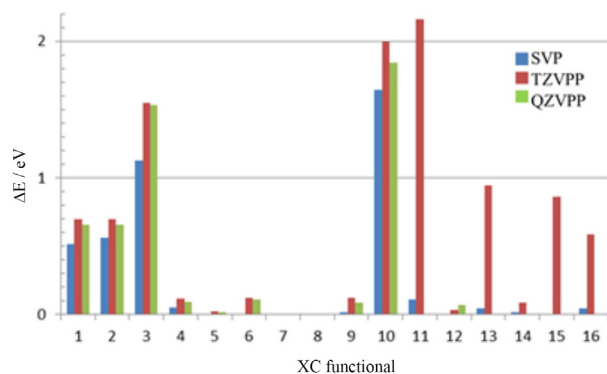


Figure S1. Energy differences (in 0.10 eV) between the two converged geometries obtained using various XC functionals and three different basis sets, SVP, TZVPP and QZVPP. There are no data for the M06, M08HX, M11, wB97 and wB97X-D functionals with the QZVPP basis set.

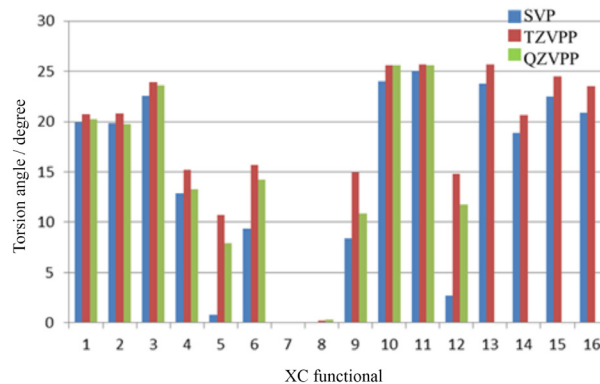


Figure S2. Torsion angles for the final distorted geometries obtained from the various XC functionals and three basis sets, SVP, TZVPP and QZVPP. There are no data for M06, M08HX, M11, wB97 and wB97X-D functionals with the QZVPP basis set.

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Table S8. Flat optimized geometry obtained from MP2/TZVPP ($E = -1100.92080122107882$ a.u.)

Element	X / a.u.	Y / a.u.	Z / a.u.
B	3.53441558302225	-0.00000046740587	0.00005913439716
B	-1.76720504566953	3.06088765304250	0.00004780684349
B	-1.76720518563751	-3.06088685503679	0.00004795453800
P	-3.34992349182739	0.00000051140197	-0.00011976177625
P	1.67496276080986	2.90112234121601	-0.00013648556192
P	1.67496262696963	-2.90112281693049	-0.00013601580638
H	5.76465035254602	0.00000095259528	0.00003143390398
H	-5.98119105958556	-0.00000168536020	0.00005583180762
H	2.99057103533313	5.17988243303073	0.00005117677193
H	-2.88230385483546	4.99234478908475	0.00002405120496
H	-2.88230431573333	-4.99234383383265	0.00002380474657
H	2.99057059460786	-5.17988302180532	0.00005106893051

BP-Coronene

Table S9. Flat optimized geometry obtained from MP2/TZVPP (E = -4395.4434425935 a.u.)

Element	X / a.u.	Y / a.u.	Z / a.u.
B	-1.76303815321243	3.04418160900955	-0.01100881806431
B	3.48206853005770	6.04972324259693	-0.00758959185755
B	-1.79705868659193	9.12027697873114	-0.00377412762967
B	-1.75481953052943	-3.04892663302791	-0.01100881806431
B	3.51785768374179	0.00474502401839	-0.01100881806431
B	-6.98024827898293	-0.00930181655016	-0.00758959185755
B	3.49817974892523	-6.04042142604677	-0.00758959185755
B	-6.99986220983563	-6.11643696404569	-0.00377412762967
B	8.79692089642757	-3.00384001468542	-0.00377412762967
B	-1.77288528504748	-9.12502365955228	-0.00435526077393
B	-7.01605965678258	6.09787552462294	-0.00435526077393
B	8.78894494183013	3.02714813492934	-0.00435526077393
P	1.73857722804430	3.02064034860788	-0.01100932273701
P	-3.51063879300097	6.06187653805009	-0.00961759338254
P	1.62573994335184	8.98883384291417	-0.00590818582380
P	-3.48523989161281	-0.00466812837644	-0.01100932273701
P	1.74666266356859	-3.01597222023143	-0.01100932273701
P	-3.49441968005575	-6.07124064727506	-0.00961759338254
P	7.00505847305676	0.00936410922496	-0.00961759338254
P	-8.59742843003691	-3.08648483056736	-0.00590818582380
P	6.97168848668507	-5.90234901234690	-0.00590818582380
P	1.64965884091492	-8.98430942444272	-0.00615084191670
P	-8.60546961748478	3.06350824841143	-0.00615084191670
P	6.95581077656986	5.92080117603128	-0.00615084191670
H	2.99182439145864	11.24575551249766	-0.00085919550211
H	-2.91201150381471	11.06282461140646	-0.00012812687678
H	-11.23502215430122	-3.03188182958370	-0.00085919550211
H	8.24319776284252	-8.21387368291396	-0.00085919550211
H	3.02219612151440	-11.23729944381127	-0.00067849641178
H	-11.24288484903056	3.00135110545539	-0.00067849641178
H	8.22068872751612	8.23594833835593	-0.00067849641178
H	-8.12468139918232	-8.05328824411928	-0.00012812687678
H	11.03669290299706	-3.00953636728716	-0.00012812687678
H	-2.88316055938480	-11.07029161571140	-0.00106412625892
H	-8.14557348681551	8.03203609547227	-0.00106412625892
H	11.02873404620033	3.03825552023911	-0.00106412625892