

# **A molecular electron density theory study of mechanism and selectivity of the intramolecular [3+2] cycloaddition reaction of a nitrone–vinylphosphonate adduct**

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## **Supplementary Information**

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**Table S1.** Values of total electronic energies  $E$  (in a.u.) in gas phase and in dichloromethane of the stationary points involved in the intramolecular 32CA reaction of nitrone–vinylphosphonate **6**

<b>System</b>	<b><math>E</math> (Gas phase)</b>	<b><math>E</math> (Dichloromethane)</b>
<b>6</b>	-1163.893271	-1163.908451
<b>TSfn</b>	-1163.879864	-1163.891554
<b>TSfx</b>	-1163.861052	-1163.871506
<b>TSbn</b>	-1163.931819	-1163.878344
<b>TSbx</b>	-1163.73104	-1163.749772
<b>7fn</b>	-1163.931819	-1163.94286
<b>7fx</b>	-1163.927257	-1163.938033
<b>7bn</b>	-1163.925414	-1163.93804
<b>7bx</b>	-1163.832592	-1163.843999

**Table S2.** Thermodynamic properties, namely, total enthalpies ( $H$ , in a.u.), entropies ( $S$  in a.u.), and free energy ( $G$ , in a.u.), computed at 298K, 1atm and in dichloromethane solvent of the stationary points involved in the intramolecular 32CA reaction of nitrone–vinylphosphonate **6**

<b>System</b>	<b><math>H</math></b>	<b><math>S</math></b>	<b><math>G</math></b>
<b>6</b>	-1163.62981	144.952	-1163.698647
<b>TSfn</b>	-1163.607578	136.435	-1163.67237
<b>TSfx</b>	-1163.593132	137.361	-1163.658364
<b>TSbn</b>	-1163.600014	138.984	-1163.666017
<b>TSbx</b>	-1163.472592	140.777	-1163.539446
<b>7fn</b>	-1163.660881	138.348	-1163.726581
<b>7fx</b>	-1163.657435	130.239	-1163.719284
<b>7bn</b>	-1163.656646	136.446	-1163.721444
<b>7bx</b>	-1163.563620	127.441	-1163.624141

**Cartesian coordinates of the stationary points involved in the intramolecular 32CA reaction of nitrono–vinylphosphonate 6, together with the imaginary frequency of transition states.**

**Nitrono–vinylphosphonate 6**

C	-1.95216700	2.92663200	0.77042300
C	-0.62349100	3.13395700	0.39986800
C	0.13221500	2.07385400	-0.10210700
C	-0.44810100	0.81496900	-0.23345400
C	-1.80059600	0.57692300	0.10445500
C	-2.52524200	1.66528700	0.63218300
C	-2.32771600	-0.77601600	-0.02431000
N	-3.55629700	-1.13662400	-0.34537400
C	-4.58606100	-0.19009500	-0.83717900
O	-3.94960800	-2.34656200	-0.31503500
O	0.26420000	-0.24246200	-0.78981700
P	1.62908800	-0.91562100	-0.20190000
O	1.99380000	-2.16296900	-0.90795300
C	1.36250200	-1.09378600	1.56950400
C	1.49743500	-2.28795000	2.15122000
O	2.67200300	0.31873000	-0.35865700
C	4.09686700	0.03583600	-0.32543200
C	4.83454000	1.31388800	-0.67298500
H	-2.53954700	3.74106700	1.18284500
H	-0.17062500	4.11523600	0.50169200
H	1.16386900	2.20843600	-0.40300300
H	-3.54194000	1.50632200	0.97390500
H	-1.67857400	-1.62234200	0.15971100
H	-5.04742500	-0.68829500	-1.68901800
H	-4.15400100	0.76543100	-1.12796000
H	-5.33733300	-0.05508400	-0.05633000
H	1.09812000	-0.20740400	2.14185800

H	1.34748200	-2.42319800	3.21896400
H	1.75964800	-3.16526100	1.56688600
H	4.36569000	-0.31595000	0.67813000
H	4.31090500	-0.76352300	-1.04005400
H	5.91415000	1.13432600	-0.65819800
H	4.55565600	1.66067800	-1.67172200
H	4.60741400	2.10535400	0.04700500

**TSfn**

Imaginary frequency= -372.68 cm<sup>-1</sup>

C	-4.03618300	-1.06090200	-0.03031700
C	-3.30927800	-2.18490500	0.37174400
C	-1.92730400	-2.11000800	0.53158500
C	-1.27120300	-0.89976100	0.30998900
C	-1.98900000	0.25214300	-0.06837000
C	-3.37560200	0.14301700	-0.25881000
O	0.09228800	-0.83354000	0.48719400
P	1.08372000	-0.51321000	-0.83657200
C	0.73933400	1.12922800	-1.40562500
C	-1.28465200	1.51907400	-0.33955000
C	1.37922800	2.27518000	-0.91476900
O	0.09174200	3.21349300	0.15784700
N	-0.69011100	2.25857800	0.60484400
O	0.99365900	-1.58997400	-1.85417000
C	-0.37681300	1.78507200	1.95407900
O	2.46308100	-0.37231000	-0.00590600
C	3.04777700	-1.54756900	0.61046300
C	4.44542400	-1.18531600	1.07393100
H	-5.11091200	-1.12430700	-0.16710800
H	-3.81804700	-3.12832100	0.54507800
H	-1.33915300	-2.97654600	0.81209000

H	-3.93379900	1.02052100	-0.57281200
H	0.34257500	1.13694700	-2.41634000
H	-1.57458300	2.09566600	-1.20934300
H	1.51814600	3.12182200	-1.57781000
H	2.13036200	2.17642300	-0.13935500
H	0.56618900	1.23045500	1.94619300
H	-1.17665300	1.14095300	2.31963100
H	-0.28309700	2.66808800	2.58616000
H	2.41349600	-1.85349000	1.44950800
H	3.06711900	-2.35862400	-0.12431700
H	4.91395100	-2.04994600	1.55484300
H	5.06659200	-0.88093500	0.22721600
H	4.41626200	-0.36346600	1.79521500

### TSfx

Imaginary frequency= -411.86 cm<sup>-1</sup>

C	2.87091500	2.70347600	0.35541900
C	1.73168800	3.48220700	0.14245800
C	0.52985800	2.89091800	-0.25724700
C	0.48437300	1.51644000	-0.46386900
C	1.64094300	0.72456000	-0.28744900
C	2.82681900	1.32459400	0.14219000
O	-0.70516700	0.92148300	-0.82724800
P	-1.25748800	-0.55234400	-0.19289800
C	-0.13927600	-0.85087200	1.11328900
C	1.46360500	-0.68205000	-0.65253200
C	0.46537700	-2.03432300	1.59136900
O	2.14838500	-1.95907700	1.11462700
N	2.10501500	-1.77276100	-0.20792900
O	-1.46231300	-1.57466400	-1.25525500
C	2.00433000	-3.01611200	-0.98819100

O	-2.61448900	-0.03235900	0.52049700
C	-3.72502000	0.40785800	-0.30041400
C	-4.91281100	0.64571000	0.61211900
H	3.79645200	3.16910200	0.67901800
H	1.77009500	4.55553400	0.30167400
H	-0.37265400	3.47602800	-0.39684800
H	3.70815900	0.70939300	0.29229100
H	0.05425100	0.04238500	1.70332400
H	1.02795300	-0.82782900	-1.64044700
H	0.67611900	-2.08537000	2.65609100
H	0.13954000	-2.98438600	1.17328500
H	2.28394900	-2.81897800	-2.02405500
H	2.69995700	-3.73042500	-0.54985000
H	0.98369600	-3.41195600	-0.95798700
H	-3.93988900	-0.36240500	-1.04787600
H	-3.43223000	1.32650600	-0.82142800
H	-5.77056400	0.99090500	0.02590700
H	-4.67936000	1.40488200	1.36402000
H	-5.19438300	-0.27638700	1.12805800

### TSbn

Imaginary frequency= -444.85 cm<sup>-1</sup>

C	3.65776500	-1.92583900	-0.16407800
C	2.65641300	-2.86452500	-0.40847900
C	1.33223400	-2.44804800	-0.48493800
C	0.98084600	-1.10391800	-0.32806400
C	1.98246900	-0.12577400	-0.10619600
C	3.31099700	-0.58810300	-0.01466600
O	-0.36289900	-0.83370800	-0.46731500
P	-1.32970200	-0.22026800	0.72106700
C	-0.71479400	1.42532300	1.04426800

C	0.51720500	1.52564200	1.68685200
C	1.82577300	1.34700900	0.08344200
N	1.11560100	2.14413600	-0.75892900
O	-0.09065600	1.78642100	-1.03277500
C	1.33230600	3.59547200	-0.71748900
O	-1.43679700	-1.13870100	1.88449000
O	-2.66888100	0.06119200	-0.11940000
C	-3.49922600	-1.05169100	-0.53625100
C	-4.83140100	-0.49258300	-0.99620800
H	4.69759500	-2.22810800	-0.09239600
H	2.89990500	-3.91566500	-0.52858600
H	0.52860500	-3.15503900	-0.65768700
H	4.09616400	0.14102000	0.16708200
H	-1.39290700	2.26114000	0.93018600
H	0.80738200	2.48161300	2.11820800
H	0.91245900	0.66212600	2.21290300
H	2.75443700	1.81354100	0.40382700
H	2.39482500	3.82397400	-0.61676700
H	0.94945400	4.01039700	-1.64963800
H	0.77113200	4.02644200	0.12110400
H	-3.62086100	-1.74023000	0.30598400
H	-2.98607500	-1.57812400	-1.34831800
H	-5.47912300	-1.30697600	-1.33636600
H	-4.69236600	0.20841200	-1.82388100
H	-5.33396000	0.03111100	-0.17831800

### TSbx

Imaginary frequency= -609.56 cm<sup>-1</sup>

C	3.23140200	2.39072100	-0.22884500
C	2.13220100	3.21922900	-0.01678100
C	0.85558600	2.67592900	-0.03948200

C	0.61157800	1.31319600	-0.27521100
C	1.73785200	0.44538600	-0.49891700
C	3.01722800	1.03816000	-0.46177900
O	-0.73572100	1.01946300	-0.34013200
P	-1.59829900	-0.07334500	0.68432000
C	-0.41807700	-1.33905800	0.53771400
C	-0.20007800	-1.61988500	-0.83346300
C	1.85009000	-1.04358400	-0.81302900
N	2.32605800	-1.87936400	0.14083600
O	2.13236700	-1.67686100	1.37106400
C	2.73417100	-3.25225800	-0.21329600
O	-1.95581300	0.56373900	1.97320200
O	-2.82592000	-0.40979800	-0.30736000
C	-4.01526000	0.42014100	-0.28499000
C	-5.14243100	-0.36276100	-0.93043300
H	4.24235200	2.78462900	-0.21212200
H	2.26363900	4.28057300	0.17048800
H	-0.01744200	3.29548900	0.13094800
H	3.87834800	0.39632100	-0.62595200
H	0.38992900	-0.72762300	0.95296500
H	0.01677700	-0.87179000	-1.59242700
H	-0.69230900	-2.48548800	-1.29108300
H	2.18115900	-1.31317000	-1.81152100
H	3.60869800	-3.49511000	0.39041300
H	2.96366000	-3.32778800	-1.27649000
H	1.91142500	-3.91940900	0.05588200
H	-3.80168300	1.34136100	-0.83901800
H	-4.24667500	0.68461300	0.75051900
H	-6.05357800	0.24391100	-0.94799500
H	-5.34709500	-1.27875100	-0.36927200
H	-4.88999200	-0.63568000	-1.95912000



### 7fn

C	3.75015200	-1.56762500	0.11331400
C	3.02322000	-2.57477200	-0.52342200
C	1.65968400	-2.41003900	-0.76099700
C	1.03794400	-1.22461500	-0.37975000
C	1.74783500	-0.18543400	0.23947100
C	3.10966600	-0.38839400	0.49229400
O	-0.32131700	-1.08698900	-0.63231100
P	-1.23334000	-0.48952500	0.60580600
C	-0.42741500	1.10712000	0.97453200
C	1.08810400	1.13320500	0.57939600
C	-0.98519000	2.33920900	0.20369800
O	0.16640500	3.08865300	-0.14867600
N	1.07424900	2.03977700	-0.60120100
O	-1.40052500	-1.41239900	1.75489600
C	2.34066900	2.70949300	-0.85256800
O	-2.57349600	-0.08549500	-0.18769000
C	-3.57649100	-1.10135200	-0.46921800
C	-4.85776100	-0.39420300	-0.86345500
H	4.80793500	-1.70012100	0.31686400
H	3.51195700	-3.49742100	-0.82108300
H	1.06400600	-3.18551400	-1.22977500
H	3.67205400	0.39538900	0.99317900
H	-0.52196200	1.23991600	2.05478600
H	1.64287200	1.60583200	1.40536600
H	-1.61330900	2.97729600	0.82849200
H	-1.53959000	2.03606800	-0.68898100
H	2.20206500	3.41928800	-1.67044000
H	3.06916600	1.95635900	-1.16029000
H	2.71823200	3.24798000	0.03174400
H	-3.20173400	-1.73341900	-1.28120700

H	-3.71104400	-1.71932600	0.42323100
H	-5.62944500	-1.13334200	-1.10077800
H	-5.22109900	0.23425100	-0.04572100
H	-4.70077100	0.23549500	-1.74359000

**7fx**

C	-2.66045500	2.78568300	-0.62623300
C	-1.59588200	3.56126800	-0.16546500
C	-0.46455800	2.95299800	0.38117000
C	-0.41970700	1.56575400	0.47175700
C	-1.49248000	0.76988700	0.03696900
C	-2.60419400	1.39365300	-0.52763700
O	0.70515600	0.98439500	1.05404000
P	1.34814700	-0.46706200	0.59765500
C	0.01597500	-1.16570500	-0.41559300
C	-1.32031900	-0.71907700	0.20420200
C	-0.21884100	-2.66905400	-0.47905100
O	-1.56935600	-2.75442600	-0.94673500
N	-2.31455200	-1.57680800	-0.45794600
O	1.83222400	-1.23522700	1.76817400
C	-3.32568700	-2.08822700	0.46312200
O	2.45158500	-0.09185200	-0.51780500
C	3.76152000	0.38557400	-0.10331100
C	4.66198200	0.38696500	-1.32264700
H	-3.53237300	3.26129000	-1.06409400
H	-1.63745900	4.64380500	-0.23766200
H	0.38006400	3.53378500	0.73554100
H	-3.41404300	0.77497600	-0.89982000
H	0.09676800	-0.75469900	-1.42679300
H	-1.28351100	-0.94363200	1.28684100
H	0.40419900	-3.18834200	-1.21099100

H	-0.08604300	-3.13399800	0.50747500
H	-3.90159300	-1.23544500	0.83701100
H	-3.99977000	-2.75080900	-0.08265300
H	-2.89686100	-2.63245600	1.31884400
H	4.14296300	-0.27206900	0.68320300
H	3.64629000	1.39372500	0.30981700
H	5.65536600	0.75576700	-1.04848100
H	4.25692400	1.03377600	-2.10579700
H	4.76773400	-0.62352500	-1.72672000

**7bn**

C	3.74830800	-1.74214400	-0.10878300
C	2.82057100	-2.71726400	-0.47163100
C	1.47284600	-2.38188900	-0.58736900
C	1.05470900	-1.07625600	-0.34121700
C	1.97062600	-0.07035300	0.01382600
C	3.31688700	-0.43719100	0.12681200
O	-0.29625300	-0.80425700	-0.53121700
P	-1.25671900	-0.23446800	0.67068200
C	-0.71501500	1.51607500	0.90096200
C	0.67844000	1.57411100	1.52889900
C	1.56919500	1.37232600	0.28205400
N	0.77828100	1.94138100	-0.85009800
O	-0.58142600	2.20902300	-0.32519100
C	1.25568200	3.25171900	-1.28073900
O	-1.26277000	-1.05166600	1.91120000
O	-2.64271900	-0.06578700	-0.11812000
C	-3.41289000	-1.23950100	-0.49252700
C	-4.78154900	-0.77140500	-0.94523700
H	4.80079200	-1.99094000	-0.01607500
H	3.13982500	-3.73728200	-0.66217300

H	0.72698800	-3.11881500	-0.86439700
H	4.04230200	0.32583500	0.39874100
H	-1.48135900	2.03017900	1.48958300
H	0.84001300	2.57029400	1.95096000
H	0.84613300	0.82722300	2.30656300
H	2.49089600	1.95244600	0.39367100
H	2.22371700	3.11109200	-1.77022900
H	0.55397500	3.65119900	-2.01548800
H	1.36157200	3.97723500	-0.45809200
H	-3.48156800	-1.90873000	0.37108200
H	-2.87981100	-1.75618900	-1.29746400
H	-5.38439100	-1.63150000	-1.25368500
H	-4.69529500	-0.08609500	-1.79277100
H	-5.30248000	-0.25647000	-0.13343600

**7bx**

C	-3.66783600	-1.96506400	-0.18567600
C	-2.72457200	-2.95111200	0.09086300
C	-1.37168700	-2.62391800	0.11290800
C	-0.93008800	-1.32372300	-0.14259100
C	-1.88765100	-0.29180100	-0.44307200
C	-3.23704400	-0.66598200	-0.44366700
O	0.47855700	-1.21644000	-0.13313100
P	1.48593100	-0.13235600	0.68022100
C	0.27197900	1.15170800	0.38994000
C	-0.09479400	1.23940900	-1.10728300
C	-1.56583100	1.18240400	-0.79131300
N	-1.67095200	2.15603000	0.41245700
O	-0.21730000	2.38637700	0.86533800
C	-2.12011000	3.48251000	0.00393500
O	1.88208800	-0.54864900	2.04367100

O	2.66859300	0.03355800	-0.39249100
C	3.84639700	-0.82098800	-0.33262500
C	4.95211700	-0.14169100	-1.11569200
H	-4.72741200	-2.19977100	-0.20042200
H	-3.03317400	-3.97157200	0.29584700
H	-0.61810000	-3.37147500	0.33428900
H	-3.97368600	0.10379100	-0.65897200
H	-0.44672900	0.48458300	0.88412400
H	0.25435800	0.44513200	-1.76079500
H	0.24682400	2.20747500	-1.47933000
H	-2.25824800	1.54163100	-1.55806500
H	-1.98005200	4.16332100	0.84587800
H	-3.19107400	3.41858500	-0.21258500
H	-1.59395300	3.88739900	-0.87353000
H	3.58342200	-1.79052300	-0.76892700
H	4.12067200	-0.97015500	0.71517700
H	5.84847800	-0.76993600	-1.10866000
H	5.20331800	0.82510600	-0.67122100
H	4.65226700	0.02025300	-2.15477200