

## Supplementary Information

### An ELF Quantum Topological Study of the Mechanism of [3+2] Cycloaddition Reactions of Nitrones with Electron-Deficient Etylenes

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#### Index

- S2 Table S1.** MPW1K/6-31G(d) total electronic energies, in gas phase and in DCM, of the stationary points involved in the stereo- and regioisomeric reaction paths of the 32CA reaction between nitrone **15** and acrolein **16**.
- S3 Table S2.** B3LYP/6-31G(d) gas phase total and relative electronic energies of the stationary points involved in the stereo- and regioisomeric reaction paths of the 32CA reaction between nitrone **15** and acrolein **16**.
- S4 Figure S1.** B3LYP/6-31G(d) geometries of the TSs involved in the 32CA reaction of nitrone **15** with acrolein **16**.
- S5** MPWB1K/6-31G(d,p) computed total electronic energies and cartesian coordinates, in gas phase, of the stationary points involved in the 32CA reaction of nitrone **15** with acrolein **16**.

**Table S1.** MPW1K/6-31G(d) total electronic energies (in au), in gas phase and in DCM, of the stationary points involved in the stereo- and regioisomeric reaction paths of the 32CA reaction between nitrene **15** and acrolein **16**.

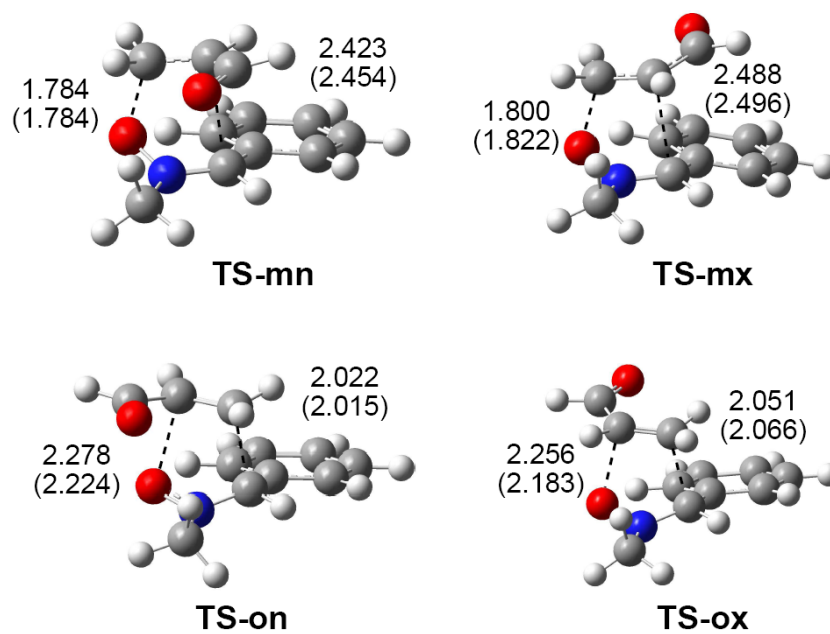
|               | Gas phase   | DCM         |
|---------------|-------------|-------------|
| <b>15</b>     | -439.947775 | -439.956442 |
| <b>16</b>     | -191.807154 | -191.812288 |
| <b>TS3-mn</b> | -631.742368 | -631.751493 |
| <b>TS3-mx</b> | -631.736041 | -631.748248 |
| <b>TS3-on</b> | -631.738547 | -631.747467 |
| <b>TS3-ox</b> | -631.733413 | -631.744391 |
| <b>17-n</b>   | -631.803442 | -631.812179 |
| <b>17-x</b>   | -631.801211 | -631.810983 |
| <b>18-n</b>   | -631.806560 | -631.813447 |
| <b>18-x</b>   | -631.800278 | -631.811268 |

<sup>a</sup> Relative to nitrene **15** and acrolein **16**.

**Table S2.** B3LYP/6-31G(d) gas phase total (E, in au) and relative<sup>a</sup> ( $\Delta E$ , in kcal/mol) electronic energies of the stationary points involved in the stereo- and regioisomeric reaction paths of the 32CA reaction between nitrone **15** and acrolein **16**.

|               | E           | $\Delta E$ |
|---------------|-------------|------------|
| <b>15</b>     | -440.179424 |            |
| <b>16</b>     | -191.911974 |            |
| <b>TS3-mn</b> | -632.071415 | 12.5       |
| <b>TS3-mx</b> | -632.065166 | 16.5       |
| <b>TS3-on</b> | -632.069194 | 13.9       |
| <b>TS3-ox</b> | -632.064312 | 17.0       |
| <b>17-n</b>   | -632.112762 | -13.4      |
| <b>17-x</b>   | -632.110678 | -12.1      |
| <b>18-n</b>   | -632.118054 | -16.7      |
| <b>18-x</b>   | -632.110072 | -11.7      |

<sup>a</sup> Relative to nitrone **15** and acrolein **16**.



**Figure S1.** B3LYP/6-31G(d) geometries of the TSs involved in the 32CA reaction of nitroene **15** with acrolein **16**. Distances are given in Angstroms. The corresponding MPWB1K/6-31G(d) lengths are given in parenthesis.

MPWB1K/6-31G(d,p) computed total electronic energies and cartesian coordinates, in gas phase, of the stationary points involved in the 32CA reaction of nitrene **15** with acrolein **16**.

**15**

E(RmPW+HF-B95) = -439.947775 au

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | 1.07026300  | -0.72949100 | -0.00010500 |
| O | 2.08623900  | 1.31392300  | 0.00010900  |
| N | 2.10419800  | 0.05707400  | 0.00000800  |
| C | 3.44699500  | -0.50910700 | 0.00002300  |
| H | 3.42386600  | -1.59227800 | -0.00022600 |
| H | 3.95269200  | -0.13338300 | -0.88225000 |
| H | 3.95250600  | -0.13378600 | 0.88257000  |
| H | 1.29052200  | -1.78312300 | -0.00017100 |
| C | -0.31134900 | -0.31645700 | -0.00005800 |
| C | -1.27562900 | -1.32781900 | 0.00008200  |
| C | -0.73476400 | 1.01462600  | -0.00012300 |
| C | -2.62019900 | -1.02635300 | 0.00011400  |
| H | -0.95797500 | -2.36122600 | 0.00015600  |
| C | -2.08568900 | 1.30568800  | -0.00010100 |
| H | 0.00282800  | 1.79690900  | -0.00020400 |
| C | -3.03118300 | 0.29634100  | 0.00001900  |
| H | -3.34877700 | -1.82281100 | 0.00021500  |
| H | -2.40197100 | 2.33792100  | -0.00017400 |
| H | -4.08367100 | 0.53631500  | 0.00004500  |

**16**

E(RmPW+HF-B95) = -191.807154 au

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -1.74428900 | 0.14224400  | 0.00002200  |
| C | -0.55861300 | -0.44988200 | 0.00000000  |
| H | -1.82695100 | 1.22085100  | 0.00010500  |
| H | -2.66854000 | -0.41408500 | -0.00003800 |
| H | -0.44312200 | -1.52378000 | -0.00008100 |
| C | 0.67090900  | 0.34688800  | 0.00009900  |
| O | 1.77725600  | -0.11980100 | -0.00008900 |
| H | 0.51252600  | 1.43992000  | 0.00000200  |

**TS-mn**

E(RmPW+HF-B95) = -631.742368 au

1 imaginary frequency = -414.8693 cm<sup>-1</sup>

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | 0.29823000  | -0.03982700 | -0.92313600 |
| N | 1.15490200  | -1.01370000 | -0.74321400 |
| C | 2.40697200  | -1.11073200 | -1.46343600 |
| H | 2.56887700  | -2.15495500 | -1.70845400 |
| H | 2.35560000  | -0.52173800 | -2.37156500 |
| H | 3.20214400  | -0.73507700 | -0.82864400 |
| O | 1.13961100  | -1.63850000 | 0.39423300  |
| C | -1.07983700 | -0.01336200 | -0.45343300 |
| C | -1.87589100 | 1.03723800  | -0.90466300 |
| C | -1.65359400 | -0.99086300 | 0.35864000  |
| C | -3.20504300 | 1.12490300  | -0.54425900 |
| H | -1.44252400 | 1.79485900  | -1.54221000 |
| C | -2.98798000 | -0.90534500 | 0.70139900  |
| H | -1.05085200 | -1.80973400 | 0.71034500  |
| C | -3.76732800 | 0.15119700  | 0.26193900  |
| H | -3.80313700 | 1.95015900  | -0.89916400 |
| H | -3.42284400 | -1.67203300 | 1.32456000  |
| H | -4.80707700 | 0.21399300  | 0.54432100  |
| H | 0.53301400  | 0.60871800  | -1.75386200 |
| C | 1.58913100  | -0.40906300 | 1.60682900  |
| H | 1.07558700  | -0.89266000 | 2.42265200  |
| H | 2.65563300  | -0.58331200 | 1.57824700  |
| C | 1.16126100  | 0.85539000  | 1.19242200  |
| H | 0.22948800  | 1.26239400  | 1.55089300  |
| C | 2.07159200  | 1.73507800  | 0.52258000  |
| O | 3.15400600  | 1.41944000  | 0.05830000  |
| H | 1.72775500  | 2.78008100  | 0.42583300  |

**TS-mx**

E(RmPW+HF-B95) = -631.736041 au

1 imaginary frequency = -423.3563 cm<sup>-1</sup>

|   |            |             |             |
|---|------------|-------------|-------------|
| C | 0.68992400 | -0.97147700 | -0.60984400 |
| N | 1.72106000 | -1.15565400 | 0.18390100  |
| C | 2.99042300 | -1.58544300 | -0.34731200 |
| H | 3.53474500 | -2.08174300 | 0.44721500  |
| H | 2.84321500 | -2.26692700 | -1.17765900 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | 3.55222000  | -0.71031300 | -0.67583700 |
| O | 1.82211600  | -0.43003700 | 1.25399900  |
| C | -0.67155700 | -0.70461700 | -0.19636200 |
| C | -1.65832700 | -0.88054600 | -1.16631900 |
| C | -1.04919200 | -0.31009500 | 1.08593900  |
| C | -2.98874900 | -0.68330200 | -0.86647500 |
| H | -1.37272700 | -1.18024100 | -2.16505600 |
| C | -2.38475400 | -0.13144600 | 1.38336900  |
| H | -0.29617900 | -0.15270500 | 1.83668900  |
| C | -3.35589800 | -0.31257300 | 0.41551400  |
| H | -3.73890600 | -0.82391400 | -1.62941100 |
| H | -2.66740000 | 0.17093700  | 2.37983800  |
| H | -4.39644500 | -0.15664600 | 0.65624100  |
| H | 0.81048700  | -1.40140400 | -1.59311700 |
| C | 0.28590500  | 2.02605900  | -0.92646200 |
| O | -0.51075900 | 2.38345400  | -0.08496300 |
| H | 0.06445500  | 2.19347000  | -1.99570100 |
| C | 2.00861800  | 1.27739900  | 0.64621000  |
| H | 1.39327900  | 1.74017900  | 1.40325100  |
| H | 3.07059900  | 1.30836900  | 0.83679900  |
| C | 1.54185200  | 1.37374600  | -0.66243100 |
| H | 2.21492500  | 1.23694300  | -1.49780500 |

**TS-on**

E(RmPW+HF-B95) = -631.738547 au

1 imaginary frequency = -462.5745 cm<sup>-1</sup>

|   |             |             |             |
|---|-------------|-------------|-------------|
| O | -1.24667000 | -0.20563100 | -1.31406300 |
| C | -0.12024700 | 0.98195000  | 0.19350100  |
| H | -0.12935100 | 1.93007000  | 0.71502300  |
| N | -1.05167900 | 0.91605700  | -0.76744500 |
| C | -2.16555400 | 1.85177600  | -0.74485400 |
| H | -2.77857400 | 1.68272700  | 0.13608100  |
| H | -1.78424600 | 2.86735700  | -0.76331700 |
| H | -2.75485500 | 1.65629900  | -1.63100800 |
| C | 1.22696300  | 0.40558800  | 0.03988400  |
| C | 2.23759700  | 0.96505100  | 0.81633800  |
| C | 1.54247000  | -0.64758300 | -0.81313500 |
| C | 3.53204200  | 0.49006300  | 0.74951900  |
| H | 2.00434100  | 1.78671000  | 1.47921200  |
| C | 2.84347400  | -1.11042400 | -0.88579300 |
| H | 0.77117300  | -1.08400000 | -1.42317500 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | 3.84045900  | -0.55218100 | -0.10590900 |
| H | 4.30024100  | 0.93912000  | 1.36047800  |
| H | 3.07741900  | -1.92156000 | -1.55872000 |
| H | 4.85115500  | -0.92625000 | -0.16495500 |
| C | -0.99646600 | -0.32622900 | 1.45141600  |
| H | -0.10290000 | -0.52341100 | 2.02295200  |
| H | -1.72680100 | 0.31861100  | 1.92400600  |
| C | -1.48934200 | -1.29912600 | 0.60714000  |
| C | -2.89545900 | -1.31336400 | 0.23172100  |
| O | -3.70550900 | -0.48424600 | 0.58113900  |
| H | -3.20433700 | -2.15635100 | -0.40452400 |
| H | -0.87969400 | -2.13583700 | 0.30448400  |

**TS-ox**

E(RmPW+HF-B95) = -631.733413 au

1 imaginary frequency = -483.7341 cm<sup>-1</sup>

|   |             |             |             |
|---|-------------|-------------|-------------|
| O | 1.69951300  | -0.04438600 | -1.20797800 |
| C | 0.49677400  | -1.19741400 | 0.28484000  |
| H | 0.51971300  | -2.10120500 | 0.87830200  |
| N | 1.46859200  | -1.15535500 | -0.63546800 |
| C | 2.63871400  | -1.97943400 | -0.44902800 |
| H | 3.30279100  | -1.48995100 | 0.26672900  |
| H | 2.36122500  | -2.96419700 | -0.09014900 |
| H | 3.14471500  | -2.05822900 | -1.40331800 |
| C | -0.85555700 | -0.67292500 | 0.05169100  |
| C | -1.86374900 | -1.14385600 | 0.88830100  |
| C | -1.18330900 | 0.22567900  | -0.95769500 |
| C | -3.16979500 | -0.72855600 | 0.72772800  |
| H | -1.61889200 | -1.84869000 | 1.67103400  |
| C | -2.49519900 | 0.62660400  | -1.12318900 |
| H | -0.41177300 | 0.60586100  | -1.60242800 |
| C | -3.49012300 | 0.15917500  | -0.28426200 |
| H | -3.93770400 | -1.10434300 | 1.38663600  |
| H | -2.73754000 | 1.32336300  | -1.91087600 |
| H | -4.51025100 | 0.48634300  | -0.41601500 |
| C | 1.46663800  | 2.23269800  | 0.09200800  |
| O | 0.36482000  | 2.64187000  | 0.35691000  |
| H | 2.10593000  | 2.77036800  | -0.62542000 |
| C | 1.33520400  | 0.22612100  | 1.52452000  |
| H | 0.39403200  | 0.61592200  | 1.88295700  |
| H | 1.86158500  | -0.44341600 | 2.19067900  |



|   |            |            |            |
|---|------------|------------|------------|
| C | 2.05594600 | 1.02304800 | 0.66243800 |
| H | 3.11809200 | 0.88894700 | 0.52457300 |

**17-n**

E(RmPW+HF-B95) = -631.803442 au

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | 0.38434900  | 0.03217600  | -0.56582200 |
| N | 0.91153300  | -1.31472500 | -0.54847300 |
| C | 2.14982800  | -1.46480600 | -1.28141600 |
| H | 2.50793900  | -2.47727500 | -1.12872100 |
| H | 1.93883700  | -1.32848500 | -2.33860700 |
| H | 2.93221600  | -0.76360600 | -0.98034600 |
| O | 1.15169100  | -1.55592800 | 0.81213400  |
| C | -1.09949000 | 0.07164000  | -0.30750100 |
| C | -1.77516700 | 1.27471400  | -0.45270100 |
| C | -1.80148600 | -1.05511500 | 0.08499600  |
| C | -3.13313400 | 1.35558600  | -0.21114200 |
| H | -1.23445700 | 2.15902100  | -0.76552000 |
| C | -3.16175700 | -0.97350400 | 0.33012200  |
| H | -1.27290000 | -1.98832300 | 0.19429100  |
| C | -3.83096600 | 0.22742900  | 0.18386400  |
| H | -3.64707200 | 2.29688200  | -0.33493700 |
| H | -3.70074500 | -1.85711800 | 0.63752800  |
| H | -4.89191100 | 0.28512900  | 0.37433000  |
| H | 0.58188500  | 0.46622500  | -1.54655400 |
| C | 1.73705300  | -0.38544900 | 1.36161500  |
| H | 1.44485000  | -0.35375200 | 2.40540400  |
| H | 2.82408600  | -0.41001800 | 1.29435400  |
| C | 1.18281700  | 0.77033400  | 0.54602000  |
| H | 0.49623700  | 1.39552100  | 1.11537100  |
| C | 2.23024800  | 1.68362400  | -0.02050500 |
| O | 3.41290600  | 1.56031500  | 0.12810100  |
| H | 1.82973900  | 2.52400400  | -0.61435200 |

**17-x**

E(RmPW+HF-B95) = -631.801211 au

|   |            |             |             |
|---|------------|-------------|-------------|
| C | 0.66808500 | -0.47753800 | -0.72942600 |
| N | 1.46602400 | -1.36430400 | 0.09841800  |
| C | 2.65309700 | -1.84124500 | -0.57321900 |
| H | 3.25839900 | -2.37592600 | 0.15064200  |
| H | 2.35089100 | -2.53405900 | -1.35360400 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | 3.25859900  | -1.04591900 | -1.02225100 |
| O | 1.85523000  | -0.55729800 | 1.18032600  |
| C | -0.77718500 | -0.45175000 | -0.31087600 |
| C | -1.76176900 | -0.28604900 | -1.27427900 |
| C | -1.14933500 | -0.56321100 | 1.02159500  |
| C | -3.09702100 | -0.22344000 | -0.91857100 |
| H | -1.48204500 | -0.21541800 | -2.31716000 |
| C | -2.48406400 | -0.50445500 | 1.37609900  |
| H | -0.38703200 | -0.70386100 | 1.77097100  |
| C | -3.46066200 | -0.33098800 | 0.41070900  |
| H | -3.85129000 | -0.09820600 | -1.68063800 |
| H | -2.76330700 | -0.59537400 | 2.41493100  |
| H | -4.50129400 | -0.28424400 | 0.69369000  |
| H | 0.72323500  | -0.83134200 | -1.75637300 |
| C | 0.44395600  | 2.07303300  | -0.53849600 |
| O | 0.44436500  | 2.89801700  | 0.32948800  |
| H | -0.25033000 | 2.15462500  | -1.38893300 |
| C | 2.20651900  | 0.71866400  | 0.67285000  |
| H | 1.94918200  | 1.45264900  | 1.42910200  |
| H | 3.27548900  | 0.77391100  | 0.46993300  |
| C | 1.38179800  | 0.89856200  | -0.58932300 |
| H | 2.02007100  | 1.05802600  | -1.46012400 |

**18-n**

E(RmPW+HF-B95) = -631.806560 au

|   |             |             |             |
|---|-------------|-------------|-------------|
| O | 2.12556600  | 1.16959900  | 0.05316600  |
| C | 0.25141100  | 0.00635100  | -0.33755300 |
| H | 0.51379600  | -0.14981200 | -1.39160000 |
| N | 0.70911000  | 1.31774000  | 0.09690600  |
| C | 0.40687300  | 2.37349200  | -0.82961500 |
| H | 0.78695600  | 2.16048200  | -1.83317000 |
| H | -0.67301100 | 2.48481500  | -0.86471500 |
| H | 0.84535300  | 3.29839200  | -0.46924900 |
| C | -1.22531000 | -0.15558600 | -0.15073000 |
| C | -1.99285000 | -0.78975900 | -1.11385900 |
| C | -1.84024300 | 0.31280300  | 1.00335300  |
| C | -3.35250400 | -0.96638900 | -0.92616500 |
| H | -1.52202800 | -1.14862400 | -2.01820500 |
| C | -3.19918100 | 0.14475100  | 1.18780100  |
| H | -1.24123900 | 0.82327200  | 1.74279200  |
| C | -3.95855700 | -0.49855400 | 0.22508300  |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | -3.93857200 | -1.46470000 | -1.68348200 |
| H | -3.66850200 | 0.51749800  | 2.08582200  |
| H | -5.01990400 | -0.63079700 | 0.37100900  |
| C | 1.11218000  | -0.89524800 | 0.53621400  |
| H | 0.63470500  | -1.04496600 | 1.49967000  |
| H | 1.31118800  | -1.86513000 | 0.09088800  |
| C | 2.38385300  | -0.06804900 | 0.67387000  |
| C | 3.57771500  | -0.65130100 | -0.03397600 |
| O | 3.76089000  | -1.82652700 | -0.16769300 |
| H | 4.28756800  | 0.09510400  | -0.42363500 |
| H | 2.64795700  | 0.08063800  | 1.72521400  |

**18-x**

E(RmPW+HF-B95) = -631.800278 au

|   |             |             |             |
|---|-------------|-------------|-------------|
| O | 1.83873800  | 0.37021400  | -0.75757100 |
| C | 0.56502900  | -1.14867700 | 0.32453600  |
| H | 0.55034800  | -2.20611200 | 0.58094000  |
| N | 1.42258000  | -0.97682800 | -0.83195500 |
| C | 2.60669900  | -1.80185100 | -0.79194800 |
| H | 3.18167700  | -1.70129500 | 0.13479400  |
| H | 2.30694300  | -2.83921300 | -0.91402000 |
| H | 3.24054000  | -1.52386500 | -1.62684400 |
| C | -0.84344100 | -0.68189200 | 0.06870900  |
| C | -1.85439000 | -1.09062500 | 0.92737700  |
| C | -1.15138800 | 0.16184900  | -0.98640200 |
| C | -3.15613900 | -0.66816300 | 0.73598100  |
| H | -1.62209100 | -1.75552300 | 1.74901600  |
| C | -2.45482600 | 0.58637700  | -1.17570900 |
| H | -0.36399800 | 0.49651600  | -1.64188900 |
| C | -3.45916900 | 0.17364600  | -0.32015800 |
| H | -3.93398100 | -1.00072700 | 1.40693900  |
| H | -2.68330700 | 1.24817900  | -1.99721800 |
| H | -4.47477900 | 0.50603600  | -0.47355800 |
| C | 1.15344900  | 2.09644700  | 0.73738100  |
| O | 0.64326300  | 2.70045200  | -0.15572900 |
| H | 1.14087700  | 2.47936000  | 1.77445000  |
| C | 1.26245000  | -0.33241800 | 1.41773700  |
| H | 0.56872300  | 0.03034500  | 2.17126200  |
| H | 2.02793400  | -0.91884600 | 1.91825700  |
| C | 1.88615300  | 0.78692300  | 0.58786100  |
| H | 2.92048300  | 0.96791700  | 0.89574400  |