Electronic Supplementary Material (ESI) for RSC Advances.


**ELECTRONIC SUPPORTING INFORMATION**

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# A new mechanistic insight on β–lactam systems formation from 5-nitroisoxazolidines

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## [1] Computational details

All calculations reported in this thesis were performed on an SGI-Altix 3700 computer in the CYFRONET regional computational centre in Cracow. Hybrid functional B3LYP [S1] with the 6-31G(d) basis set included in the GAUSSIAN 09 [S2] package was used. Subsequently, similar simulations using more advanced B3LYP/6-31G(d,p), B3LYP/6-31+G(d) as well as B3LYP/6-31++G(d) theoretical levels were performed. For the calculations of solvent effect on the reaction paths, the polarizable continuum model (PCM), in which the cavity is created via a series of overlapping spheresm, was used.

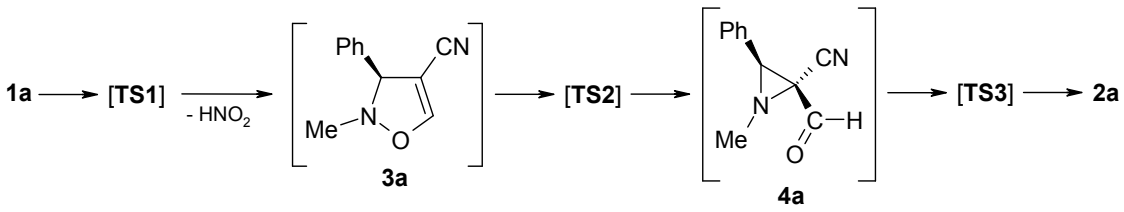
Transition states were calculated using the QST2 (or QST3) and TS procedures. Subsequently, transition states were localized out by changing gradually the distance between the centers (with optimization after each step). In this way transition states identical as previously have been obtained. Stationary points were characterized by frequency calculations. All reactants, and products, had positive Hessian matrices. All transition states showed only one negative eigenvalue in their diagonalized Hessian matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction

coordinate under consideration. For all reactions, intrinsic reaction coordinate (IRC) calculations were performed to connect previously computed transition structures (**TS**) with suitable minima.

# [2] Selected results of quantumchemical calculations

## Energetic aspects

**Table ESI-01**. Kinetic and thermodynamic parameters for conversion of *3,4-trans-4,5-trans*-2-methyl-3-phenyl-4-cyano-5-nitroisoxazolidine (**1a**) into *3,4-trans*-1-methyl-3-cyano-4-phenyl-2-azetidinone (**2a**) in methanol solution according to DFT calculations (T = 298 K; ΔH, ΔG in kcal/mol; ΔS in cal/molK)




| Theory level | Transition | ΔH | ΔG | ΔS |
|---|---|---|---|---|
| B3LYP/6-31G(d) | **1a→TS1** | 28.7 | 28.2 | 1.7 |
| | **1a→3a**+$HNO_2$ | 9.7 | -3.5 | 44.4 |
| | **3a→TS2** | 32.4 | 32.0 | 1.2 |
| | **3a→4a** | -14.8 | -15.1 | 1.3 |
| | **4a→TS3** | 71.7 | 71.8 | -0.3 |
| | **4a→2a** | -31.9 | -32.2 | 1.2 |
| B3LYP/6-31G(d,p) | **1a→TS1** | 27.1 | 26.9 | 0.8 |
| | **1a→3a**+$HNO_2$ | 7.4 | -5.7 | 43.9 |
| | **3a→TS2** | 32.3 | 31.9 | 1.3 |
| | **3a→4a** | -14.8 | -15.1 | 1.2 |
| | **4a→TS3** | 71.7 | 71.8 | -0.3 |
| | **4a→2a** | -31.8 | -32.2 | 1.2 |
| B3LYP/6-31+G(d) | **1a→TS1** | 25.5 | 23.0 | 8.5 |
| | **1a→3a**+$HNO_2$ | 5.9 | -9.0 | 50.1 |
| | **3a→TS2** | 30.5 | 30.6 | -0.1 |
| | **3a→4a** | -14.7 | -15.1 | 1.2 |
| | **4a→TS3** | 70.0 | 70.3 | -0.9 |
| | **4a→2a** | -33.3 | -33.4 | 0.4 |
| B3LYP/6-31++G(d) | **1a→TS1** | 25.6 | 23.0 | 8.5 |
| | **1a→3a**+$HNO_2$ | 5.9 | -9.0 | 50.0 |
| | **3a→TS2** | 30.6 | 30.6 | 0.0 |
| | **3a→4a** | -14.7 | -15.0 | 1.2 |
| | **4a→TS3** | 70.0 | 70.3 | -0.9 |
| | **4a→2a** | -33.3 | -33.5 | 0.6 |

**Cartesian coordinates for key structures of conversion of *3,4-trans-4,5-trans*-2-methyl-3-phenyl-4-cyano-5-nitroisoxazolidine (1a) into *3,4-trans*-1-methyl-3-cyano-4-phenyl-2-azetidinone (2a) in methanol solution according to B3LYP/6-31G(d) calculations**

[**TS1**]

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.958437 | -0.285758 | 0.958540 |
| 2 | 6 | 0 | -2.126043 | -0.908335 | 0.405925 |
| 3 | 8 | 0 | -1.885698 | -1.606002 | -0.657376 |
| 4 | 7 | 0 | -0.465295 | -1.352632 | -1.054658 |
| 5 | 6 | 0 | 0.202168 | -1.020123 | 0.232407 |
| 6 | 6 | 0 | 1.467064 | -0.221408 | -0.005500 |
| 7 | 6 | 0 | 2.649814 | -0.616566 | 0.629745 |
| 8 | 6 | 0 | 1.477576 | 0.905247 | -0.841025 |
| 9 | 6 | 0 | 3.828691 | 0.109433 | 0.444338 |
| 10 | 6 | 0 | 2.656766 | 1.624886 | -1.029614 |
| 11 | 6 | 0 | 3.834212 | 1.230340 | -0.386766 |
| 12 | 1 | 0 | 0.452333 | -1.937469 | 0.788420 |
| 13 | 1 | 0 | -3.129084 | -0.974745 | 0.807364 |
| 14 | 1 | 0 | 2.650102 | -1.493191 | 1.272551 |
| 15 | 1 | 0 | 0.565376 | 1.216751 | -1.339056 |
| 16 | 6 | 0 | -0.006374 | -2.591936 | -1.676342 |
| 17 | 1 | 0 | -0.612944 | -2.791715 | -2.561401 |
| 18 | 1 | 0 | 1.024736 | -2.410984 | -1.991193 |
| 19 | 1 | 0 | -0.035253 | -3.449321 | -0.991204 |
| 20 | 1 | 0 | 4.739716 | -0.205465 | 0.945078 |
| 21 | 1 | 0 | 4.750810 | 1.794178 | -0.535663 |
| 22 | 1 | 0 | 2.656611 | 2.495358 | -1.679575 |
| 23 | 1 | 0 | -1.110833 | 0.923878 | 0.460430 |
| 24 | 7 | 0 | -2.729913 | 1.302569 | -0.504884 |
| 25 | 8 | 0 | -1.667853 | 1.956172 | -0.153850 |
| 26 | 8 | 0 | -3.572766 | 1.901768 | -1.145558 |
| 27 | 6 | 0 | -0.877382 | -0.111021 | 2.383891 |
| 28 | 7 | 0 | -0.780416 | 0.068445 | 3.528818 |

[**3a**]

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.484235 | 0.972585 | 0.009324 |
| 2 | 6 | 0 | -2.602384 | 0.503914 | -0.580349 |
| 3 | 8 | 0 | -2.686687 | -0.826655 | -0.632496 |
| 4 | 7 | 0 | -1.363850 | -1.349625 | -0.189408 |
| 5 | 6 | 0 | -0.677567 | -0.221552 | 0.513992 |
| 6 | 6 | 0 | 0.805337 | -0.204892 | 0.185990 |
| 7 | 6 | 0 | 1.745408 | -0.160453 | 1.220539 |
| 8 | 6 | 0 | 1.249415 | -0.216783 | -1.143277 |
| 9 | 6 | 0 | 3.113030 | -0.122741 | 0.934847 |
| 10 | 6 | 0 | 2.613363 | -0.182575 | -1.429600 |
| 11 | 6 | 0 | 3.548969 | -0.133841 | -0.390708 |
| 12 | 1 | 0 | -0.793801 | -0.308328 | 1.607909 |
| 13 | 1 | 0 | -3.436789 | 1.039314 | -1.016954 |
| 14 | 1 | 0 | 1.407178 | -0.156403 | 2.254172 |
| 15 | 1 | 0 | 0.522886 | -0.260922 | -1.949369 |
| 16 | 6 | 0 | -1.657905 | -2.486349 | 0.676196 |
| 17 | 1 | 0 | -2.207275 | -3.238930 | 0.106329 |
| 18 | 1 | 0 | -0.695818 | -2.910217 | 0.978506 |
| 19 | 1 | 0 | -2.228495 | -2.206178 | 1.573493 |
| 20 | 1 | 0 | 3.833420 | -0.088925 | 1.747453 |
| 21 | 1 | 0 | 4.611637 | -0.106979 | -0.615640 |
| 22 | 1 | 0 | 2.948174 | -0.193676 | -2.463286 |
| 23 | 6 | 0 | -1.150731 | 2.325250 | 0.220991 |
| 24 | 7 | 0 | -0.848125 | 3.436641 | 0.407935 |

[**TS2**]

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.486783 | 0.858308 | 0.231380 |
| 2 | 6 | 0 | -2.903998 | 0.701048 | 0.181586 |
| 3 | 8 | 0 | -3.477292 | -0.376134 | -0.023205 |
| 4 | 7 | 0 | -1.142190 | -1.233697 | -0.655806 |
| 5 | 6 | 0 | -0.682158 | -0.418341 | 0.404795 |
| 6 | 6 | 0 | 0.835410 | -0.268239 | 0.177430 |
| 7 | 6 | 0 | 1.706327 | -0.708223 | 1.179914 |
| 8 | 6 | 0 | 1.349524 | 0.246093 | -1.021896 |
| 9 | 6 | 0 | 3.086769 | -0.594177 | 1.001314 |
| 10 | 6 | 0 | 2.728540 | 0.349692 | -1.196502 |
| 11 | 6 | 0 | 3.599597 | -0.067531 | -0.185673 |
| 12 | 1 | 0 | -0.838685 | -0.850052 | 1.403153 |
| 13 | 1 | 0 | -3.495906 | 1.605071 | 0.414985 |
| 14 | 1 | 0 | 1.309862 | -1.120945 | 2.102922 |
| 15 | 1 | 0 | 0.675277 | 0.560316 | -1.811564 |
| 16 | 6 | 0 | -1.590320 | -2.555636 | -0.355756 |
| 17 | 1 | 0 | -2.464250 | -2.800580 | -0.968951 |
| 18 | 1 | 0 | -0.781757 | -3.216108 | -0.726047 |
| 19 | 1 | 0 | -1.781138 | -2.765709 | 0.702020 |
| 20 | 1 | 0 | 3.757579 | -0.918132 | 1.791760 |
| 21 | 1 | 0 | 4.673668 | 0.015442 | -0.324628 |
| 22 | 1 | 0 | 3.122692 | 0.754342 | -2.124162 |
| 23 | 6 | 0 | -0.893422 | 2.128364 | 0.167951 |
| 24 | 7 | 0 | -0.408656 | 3.193308 | 0.115648 |

[**4a**]

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.521100 | 0.419823 | -0.215588 |
| 2 | 6 | 0 | 2.701904 | 0.021737 | -1.057341 |
| 3 | 8 | 0 | 3.176179 | -1.096944 | -1.067999 |
| 4 | 7 | 0 | 1.280673 | -0.115902 | 1.143178 |
| 5 | 6 | 0 | 0.484839 | -0.692823 | 0.105190 |
| 6 | 6 | 0 | -0.986283 | -0.455752 | 0.055787 |
| 7 | 6 | 0 | -1.743142 | -1.104208 | -0.930574 |
| 8 | 6 | 0 | -1.627598 | 0.390604 | 0.970138 |
| 9 | 6 | 0 | -3.121277 | -0.903573 | -1.006494 |
| 10 | 6 | 0 | -3.006426 | 0.588859 | 0.893086 |
| 11 | 6 | 0 | -3.755757 | -0.055031 | -0.095182 |
| 12 | 1 | 0 | 0.818764 | -1.650779 | -0.299459 |
| 13 | 1 | 0 | 3.118319 | 0.833254 | -1.683080 |
| 14 | 1 | 0 | -1.250991 | -1.768183 | -1.637112 |
| 15 | 1 | 0 | -1.041640 | 0.878935 | 1.742178 |
| 16 | 6 | 0 | 2.313088 | -0.913399 | 1.815593 |
| 17 | 1 | 0 | 3.068418 | -0.234183 | 2.219699 |
| 18 | 1 | 0 | 1.821724 | -1.425532 | 2.647575 |
| 19 | 1 | 0 | 2.795656 | -1.651557 | 1.167813 |
| 20 | 1 | 0 | -3.699002 | -1.411509 | -1.773538 |
| 21 | 1 | 0 | -4.829624 | 0.099622 | -0.152127 |
| 22 | 1 | 0 | -3.496730 | 1.243372 | 1.608354 |
| 23 | 6 | 0 | 1.079843 | 1.786579 | -0.405177 |
| 24 | 7 | 0 | 0.737030 | 2.882364 | -0.582168 |

[**TS3**]

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.349300 | 0.778834 | -0.644205 |
| 2 | 6 | 0 | 2.620688 | 0.343883 | 0.320880 |
| 3 | 8 | 0 | 3.768130 | -0.026298 | 0.046368 |
| 4 | 7 | 0 | 1.470268 | -0.891744 | 0.488308 |
| 5 | 6 | 0 | 0.517422 | -0.456328 | -0.586866 |
| 6 | 6 | 0 | -0.946900 | -0.372406 | -0.229394 |
| 7 | 6 | 0 | -1.905406 | -0.533166 | -1.236760 |
| 8 | 6 | 0 | -1.360386 | -0.116877 | 1.084660 |
| 9 | 6 | 0 | -3.264843 | -0.429831 | -0.936442 |
| 10 | 6 | 0 | -2.719537 | -0.020484 | 1.383207 |
| 11 | 6 | 0 | -3.674084 | -0.173773 | 0.373889 |
| 12 | 1 | 0 | 0.658150 | -1.085631 | -1.472197 |
| 13 | 1 | 0 | 2.463924 | 1.057301 | 1.159021 |
| 14 | 1 | 0 | -1.589663 | -0.739626 | -2.256351 |
| 15 | 1 | 0 | -0.618194 | -0.012133 | 1.870357 |
| 16 | 6 | 0 | 2.144948 | -2.133301 | 0.114701 |
| 17 | 1 | 0 | 2.844286 | -2.392085 | 0.913707 |
| 18 | 1 | 0 | 1.370876 | -2.901300 | 0.007502 |
| 19 | 1 | 0 | 2.714226 | -2.059570 | -0.821030 |
| 20 | 1 | 0 | -4.001516 | -0.556798 | -1.724535 |
| 21 | 1 | 0 | -4.731993 | -0.099245 | 0.609293 |
| 22 | 1 | 0 | -3.032802 | 0.171071 | 2.405609 |
| 23 | 6 | 0 | 0.757885 | 2.013916 | -0.260473 |
| 24 | 7 | 0 | 0.338753 | 3.095403 | -0.111377 |

[**2a**]

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.429731 | 0.711609 | 0.549889 |
| 2 | 6 | 0 | 2.121114 | -0.685459 | 0.389690 |
| 3 | 8 | 0 | 3.113439 | -1.208867 | 0.850529 |
| 4 | 7 | 0 | 1.164971 | -1.093106 | -0.483553 |
| 5 | 6 | 0 | 0.429068 | 0.184280 | -0.554736 |
| 6 | 6 | 0 | -1.038802 | 0.142892 | -0.211565 |
| 7 | 6 | 0 | -1.938137 | 0.945191 | -0.924169 |
| 8 | 6 | 0 | -1.521865 | -0.672301 | 0.822226 |
| 9 | 6 | 0 | -3.297256 | 0.943373 | -0.604038 |
| 10 | 6 | 0 | -2.880123 | -0.677834 | 1.139527 |
| 11 | 6 | 0 | -3.770870 | 0.131569 | 0.428587 |
| 12 | 1 | 0 | 0.582585 | 0.688317 | -1.514859 |
| 13 | 1 | 0 | 0.958599 | 0.835654 | 1.528921 |
| 14 | 1 | 0 | -1.572861 | 1.573576 | -1.732901 |
| 15 | 1 | 0 | -0.836698 | -1.309676 | 1.375235 |
| 16 | 6 | 0 | 1.016120 | -2.317156 | -1.241972 |
| 17 | 1 | 0 | 1.759502 | -3.030673 | -0.880217 |
| 18 | 1 | 0 | 0.015210 | -2.735613 | -1.098988 |
| 19 | 1 | 0 | 1.180250 | -2.135674 | -2.310128 |
| 20 | 1 | 0 | -3.984281 | 1.570978 | -1.164672 |
| 21 | 1 | 0 | -4.828707 | 0.125318 | 0.676002 |
| 22 | 1 | 0 | -3.243515 | -1.315734 | 1.940348 |
| 23 | 6 | 0 | 2.233675 | 1.874658 | 0.223495 |
| 24 | 7 | 0 | 2.887384 | 2.795898 | -0.048529 |

## [3] References

[S1] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.

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