Supporting Information: Ammonia Evolution in Glycine Pyrolysis via Ionic-Pair Reaction Mechanisms

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Contents

1 Cartesian coordinates of all the stationary points

The full Cartesian coordinate dataset and related computational files are publicly accessible via Zenodo at https://zenodo.org/records/15340633.

2 CREST input command lines and example output

Minimum input In the case of a covalently bonded molecule, the command line to start the calculation is:

```
crest input.xyz
```

while in case we want to sample a molecular aggregate is:

```
crest input.xyz --nci
```

where `input.xyz` file is:

```
20


O            2.81204560743322      -0.88432722067055      -0.56662624129711
H            3.57046987506096      -1.46251566756047      -0.38758948098719
C            2.82729124138263       0.15728476153218       0.26736779327982
C            1.64911548063984       1.08851824088157       0.08347444164661
O            3.70116803065221       0.32513244971914       1.07660854973184
N            0.84411773523699       0.74240231156616      -1.07010038561584
H            2.04672855149321       2.11708332603840       0.08151908909250
H            1.02410805144401       0.98478792674369       0.97674027090000
H           -0.01093060341502       1.28903841363415      -1.06487439341897
H            1.34693957633043       0.91244003869019      -1.93340684920228
O           -1.92976509949508       1.16944454159219      -0.05442686570009
```

```
H          -4.16008618641667        1.16749964920928        0.59008248616907
C          -2.61184925230803        0.18495175887943        0.05938821904584
C          -2.18785017078367       -1.23543632727538       -0.23662682413783
O          -3.89487991600212        0.24740687095036        0.42807567581179
N          -0.80585140315431       -1.47008143838764        0.12278692912895
H          -2.41132150285016       -1.38409563090288       -1.31196771606087
H          -2.83480738218097       -1.91006352356507        0.33160343963413
H          -0.51658618684671       -2.38687919952370       -0.19857081024016
H          -0.19724344621921       -0.77975128155122       -0.31908132777973
```

Transition state input In the case of a transition state, we first have to constrain the coordinates of the atom involved in the reactive mode. Supposing that we want to constrain atoms 2,3 and 6, the command line is:

```
crest input.xyz --constrain 2,3,6
```

This produces the file `.xcontrol.sample` which must be renamed to `constraints.inp` and finally run the command:

```
crest input.xyz --cinp constraints.inp --subrmsd
```

Example output

```
      ___ ___ ___ ___ _____
     / __| _ \ __/ __|_   _|
    | (__|   / _|\__ \ | |
     \___|_|_\___|___/ |_|

Conformer-Rotamer Ensemble Sampling Tool
        based on the xTB methods
```

```
    Version 3.0.2, Thu, 29 August 14:20:46, 08/29/2024
    commit (65685a7) compiled by 'usr@d37571da525e'

Cite work conducted with this code as

• P.Pracht, F.Bohle, S.Grimme, PCCP, 2020, 22, 7169-7192.
• S.Grimme, JCTC, 2019, 15, 2847-2862.
• P.Pracht, S.Grimme, C.Bannwarth, F.Bohle, S.Ehlert,
  G.Feldmann, J.Gorges, M.Müller, T.Neudecker, C.Plett,
  S.Spicher, P.Steinbach, P.Weso␣lowski, F.Zeller,
  J. Chem. Phys., 2024, 160, 114110.

for works involving QCG cite

• S.Spicher, C.Plett, P.Pracht, A.Hansen, S.Grimme,
  JCTC, 2022, 18 (5), 3174-3189.
• C.Plett, S. Grimme,
  Angew. Chem. Int. Ed. 2023, 62, e202214477.

for works involving MECP screening cite

• P.Pracht, C.Bannwarth, JCTC, 2022, 18 (10), 6370-6385.

Original code
  P.Pracht, S.Grimme, Universität Bonn, MCTC
with help from (alphabetical order):
```

```
     C.Bannwarth, F.Bohle, S.Ehlert, G.Feldmann, J.Gorges,
     S.Grimme, C.Plett, P.Pracht, S.Spicher, P.Steinbach,
     P.Wesolowski, F.Zeller

   Online documentation is available at
   https://crest-lab.github.io/crest-docs/

   This program is distributed in the hope that it will be useful,
   but WITHOUT ANY WARRANTY; without even the implied warranty of
   MERCHANTABILITY or FITNESS FOR A PARTICULAR PURPOSE. See the
   GNU Lesser General Public License (LGPL) for more details.

 Command line input:
 $ crest 2gly.xyz --temp 473.15 -T 4

  -T 4 (CPUs/Threads selected)

> Setting up backup calculator ... done.
 ----------------
 Calculation info
 ----------------
> User-defined calculation level:
 : xTB calculation via tblite lib
 : GFN2-xTB level
 :   Molecular charge    : 0
 :   Fermi temperature   : 300.00000
 :   Accuracy            : 1.00000
```

```
:   max SCC cycles      : 500


-----------------------------
Initial Geometry Optimization
-----------------------------
Geometry successfully optimized.


                    CREST iMTD-GC SAMPLING

Input structure:
 20

O          2.7544627454       -1.0050182697       -0.5158876247
H          3.5067553102       -1.5779323851       -0.2981697777
C          2.7970063328        0.1035154559        0.2256244947
C          1.6308096029        1.0349811031       -0.0228334038
O          3.6839644562        0.3254129998        1.0071727539
N          0.8058627791        0.6055294054       -1.1334339391
H          2.0450396977        2.0527687301       -0.1169926021
H          1.0159308503        1.0182841868        0.8831336633
H         -0.0398450327        1.1655217284       -1.1661957717
H          1.3006625920        0.6918730941       -2.0138393743
O         -1.9501585428        1.1635954235       -0.1305243694
H         -4.1730450995        1.2549525611        0.5324539825
C         -2.6464342668        0.2042116129        0.0753325782
```

```
C         -2.2481216216       -1.2435641537       -0.0984671573
O         -3.9239655721        0.3198752827        0.4504996334
N         -0.8655670551       -1.4681280042        0.2653291369
H         -2.4867915621       -1.4819010361       -1.1541971200
H         -2.8987261831       -1.8549769326        0.5335937541
H         -0.5936239028       -2.4136127910        0.0213745334
H         -0.2520180291       -0.8285420743       -0.2414107844

------------------------------------------------
Generating MTD length from a flexibility measure
------------------------------------------------
Calculating GFN0-xTB WBOs   ... done.
Calculating NCI flexibility ... done.
    covalent flexibility measure :   0.287
non-covalent flexibility measure :   0.295
flexibility measure :   0.222
t(MTD) / ps    :     5.0
Sum(t(MTD)) / ps :    70.0 (14 MTDs)

-----------------------------------
Starting trial MTD to test settings
-----------------------------------
Trial MTD 1 runtime (1.0 ps) ...        0 min,  2.298 sec
Estimated runtime for one MTD (5.0 ps) on a single thread: 11 sec
Estimated runtime for a batch of 14 MTDs on 4 threads: 46 sec

*********************************************************************************
```

```
**                        N E W   I T E R A T I O N   C Y C L E
********************************************************************************

 ------------------------------
 Meta-Dynamics Iteration 1
 ------------------------------
 list of applied metadynamics Vbias parameters:
$metadyn    0.06000   1.300
$metadyn    0.03000   1.300
$metadyn    0.01500   1.300
$metadyn    0.06000   0.780
$metadyn    0.03000   0.780
$metadyn    0.01500   0.780
$metadyn    0.06000   0.468
$metadyn    0.03000   0.468
$metadyn    0.01500   0.468
$metadyn    0.06000   0.281
$metadyn    0.03000   0.281
$metadyn    0.01500   0.281
$metadyn    0.02000   0.100
$metadyn    0.10000   0.800

  :::::::::::::: starting MTD    9 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
```

```
|   SHAKE algorithm      : true (all bonds) |
|   dump interval(Vbias) :    1.00 ps       |
|   Vbias prefactor (k)  :  0.0150 Eh       |
|   Vbias exponent (alpha)   :  0.4680 bohr-2   |
:::::::::::::: starting MTD   12 ::::::::::::::
|   MD simulation time   :     5.0 ps       |
|   target T             :   300.0 K        |
|   timestep dt          :     5.0 fs       |
|   dump interval(trj)   :   100.0 fs       |
|   SHAKE algorithm      : true (all bonds) |
|   dump interval(Vbias) :    1.00 ps       |
|   Vbias prefactor (k)  :  0.0150 Eh       |
|   Vbias exponent (alpha)   :  0.2808 bohr-2   |
:::::::::::::: starting MTD    1 ::::::::::::::
|   MD simulation time   :     5.0 ps       |
|   target T             :   300.0 K        |
|   timestep dt          :     5.0 fs       |
|   dump interval(trj)   :   100.0 fs       |
|   SHAKE algorithm      : true (all bonds) |
|   dump interval(Vbias) :    1.00 ps       |
|   Vbias prefactor (k)  :  0.0600 Eh       |
|   Vbias exponent (alpha)   :  1.3000 bohr-2   |
:::::::::::::: starting MTD    5 ::::::::::::::
|   MD simulation time   :     5.0 ps       |
|   target T             :   300.0 K        |
|   timestep dt          :     5.0 fs       |
|   dump interval(trj)   :   100.0 fs       |
```

```
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0300 Eh       |
  |   Vbias exponent (alpha)   :  0.7800 bohr-2   |
*MTD   1 completed successfully ...        0 min, 11.821 sec
  :::::::::::::: starting MTD    2 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0300 Eh       |
  |   Vbias exponent (alpha)   :  1.3000 bohr-2   |
*MTD  12 completed successfully ...        0 min, 12.278 sec
  :::::::::::::: starting MTD   13 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0200 Eh       |
  |   Vbias exponent (alpha)   :  0.1000 bohr-2   |
*MTD   9 completed successfully ...        0 min, 12.512 sec
  :::::::::::::: starting MTD   10 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
```

```
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0600 Eh       |
  |   Vbias exponent (alpha)   :  0.2808 bohr-2   |
*MTD   5 completed successfully ...        0 min, 12.637 sec
  :::::::::::::: starting MTD    6 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0150 Eh       |
  |   Vbias exponent (alpha)   :  0.7800 bohr-2   |
*MTD  10 completed successfully ...        0 min, 11.503 sec
  :::::::::::::: starting MTD   11 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0300 Eh       |
  |   Vbias exponent (alpha)   :  0.2808 bohr-2   |
```

```
*MTD   2 completed successfully ...        0 min, 12.820 sec
  :::::::::::::: starting MTD    3 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0150 Eh       |
  |   Vbias exponent (alpha)   :  1.3000 bohr-2   |
*MTD  13 completed successfully ...        0 min, 12.676 sec
  :::::::::::::: starting MTD   14 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.1000 Eh       |
  |   Vbias exponent (alpha)   :  0.8000 bohr-2   |
*MTD   6 completed successfully ...        0 min, 14.488 sec
  :::::::::::::: starting MTD    7 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
```

```
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0600 Eh       |
  |   Vbias exponent (alpha)   :  0.4680 bohr-2   |
*MTD  11 completed successfully ...        0 min, 16.289 sec
*MTD  14 completed successfully ...        0 min, 16.403 sec
*MTD   3 completed successfully ...        0 min, 18.077 sec
  :::::::::::::: starting MTD    4 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0600 Eh       |
  |   Vbias exponent (alpha)   :  0.7800 bohr-2   |
*MTD   7 completed successfully ...        0 min, 15.767 sec
  :::::::::::::: starting MTD    8 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0300 Eh       |
  |   Vbias exponent (alpha)   :  0.4680 bohr-2   |
*MTD   4 completed successfully ...        0 min, 12.252 sec
*MTD   8 completed successfully ...        0 min, 12.148 sec
```

```
 ====================================
 |  Multilevel Ensemble Optimization  |
 ====================================
 Optimizing all 686 structures from file "crest_dynamics.trj" ...
 ----------------------
 crude pre-optimization
 ----------------------
 Optimization engine: ANCOPT
 Hessian update type: BFGS
 E/G convergence criteria:  0.500E-03 Eh, 0.100E-01 Eh/a0
 maximum optimization steps: 200
 |>0.1% |>10.1% |>20.1% |>30.0% |>40.1% |>50.0% |>60.1% |>70.1% |>80.0% |>90.1% |>100.0%
 done.
> 686 of 686 structures successfully optimized (100.0% success)
> Total runtime for 686 optimizations:
 * wall-time:     0 d,  0 h,  0 min, 25.712 sec
 *  cpu-time:     0 d,  0 h,  1 min, 42.142 sec
 * ratio c/w:     3.973 speedup
> Corresponding to approximately 0.037 sec per processed structure

CREGEN> running RMSDs ... done.
CREGEN> E lowest :   -35.77959
 71 structures remain within    12.00 kcal/mol window
 ----------------------------------
 optimization with tight thresholds
 ----------------------------------
```

```
 Optimization engine: ANCOPT
 Hessian update type: BFGS
 E/G convergence criteria:  0.100E-05 Eh, 0.800E-03 Eh/a0
 maximum optimization steps: 200
 |>1.4% |>11.3% |>21.1% |>31.0% |>40.8% |>50.7% |>60.6% |>70.4% |>80.3% |>90.1% |>100.0%
 done.
> 71 of 71 structures successfully optimized (100.0% success)
> Total runtime for 71 optimizations:
 * wall-time:     0 d,  0 h,  0 min, 14.114 sec
 *  cpu-time:     0 d,  0 h,  0 min, 54.102 sec
 * ratio c/w:     3.833 speedup
> Corresponding to approximately 0.199 sec per processed structure

CREGEN> running RMSDs ... done.
CREGEN> E lowest :   -35.78144
 10 structures remain within     6.00 kcal/mol window


 ------------------------------
 Meta-Dynamics Iteration 2
 ------------------------------
 list of applied metadynamics Vbias parameters:
$metadyn    0.06000   1.300
$metadyn    0.03000   1.300
$metadyn    0.01500   1.300
$metadyn    0.06000   0.780
$metadyn    0.03000   0.780
$metadyn    0.01500   0.780
```

```
$metadyn    0.06000   0.468
$metadyn    0.03000   0.468
$metadyn    0.01500   0.468
$metadyn    0.06000   0.281
$metadyn    0.03000   0.281
$metadyn    0.01500   0.281
$metadyn    0.02000   0.100
$metadyn    0.10000   0.800


  ::::::::::::: starting MTD    5 :::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0300 Eh       |
  |   Vbias exponent (alpha)   :  0.7800 bohr-2   |
  ::::::::::::: starting MTD   12 :::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0150 Eh       |
  |   Vbias exponent (alpha)   :  0.2808 bohr-2   |
```

```
  :::::::::::::: starting MTD    1 ::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0600 Eh       |
  |   Vbias exponent (alpha)   :  1.3000 bohr-2   |
  :::::::::::::: starting MTD    9 ::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0150 Eh       |
  |   Vbias exponent (alpha)   :  0.4680 bohr-2   |
*MTD   5 completed successfully ...        0 min, 18.840 sec
  :::::::::::::: starting MTD    6 ::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0150 Eh       |
```

```
  |   Vbias exponent (alpha)   :  0.7800 bohr-2   |
*MTD   1 completed successfully ...        0 min, 19.580 sec
  :::::::::::: starting MTD    2 ::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0300 Eh       |
  |   Vbias exponent (alpha)   :  1.3000 bohr-2   |
*MTD  12 completed successfully ...        0 min, 19.965 sec
  :::::::::::: starting MTD   13 ::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0200 Eh       |
  |   Vbias exponent (alpha)   :  0.1000 bohr-2   |
*MTD   9 completed successfully ...        0 min, 21.748 sec
  :::::::::::: starting MTD   10 ::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
```

```
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0600 Eh       |
  |   Vbias exponent (alpha)   :  0.2808 bohr-2   |
*MTD  13 completed successfully ...        0 min, 17.660 sec
  :::::::::::::: starting MTD   14 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.1000 Eh       |
  |   Vbias exponent (alpha)   :  0.8000 bohr-2   |
*MTD   6 completed successfully ...        0 min, 19.244 sec
  :::::::::::::: starting MTD    7 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0600 Eh       |
  |   Vbias exponent (alpha)   :  0.4680 bohr-2   |
*MTD   2 completed successfully ...        0 min, 19.715 sec
  :::::::::::::: starting MTD    3 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
```

```
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0150 Eh       |
  |   Vbias exponent (alpha)   :  1.3000 bohr-2   |
*MTD  10 completed successfully ...        0 min, 18.036 sec
  :::::::::::::: starting MTD   11 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0300 Eh       |
  |   Vbias exponent (alpha)   :  0.2808 bohr-2   |
*MTD   7 completed successfully ...        0 min, 19.527 sec
  :::::::::::::: starting MTD    8 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0300 Eh       |
  |   Vbias exponent (alpha)   :  0.4680 bohr-2   |
```

```
*MTD  14 completed successfully ...        0 min, 20.091 sec
*MTD   3 completed successfully ...        0 min, 20.309 sec
  :::::::::::::: starting MTD    4 ::::::::::::::
  |   MD simulation time   :     5.0 ps       |
  |   target T             :   300.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  |   dump interval(Vbias) :    1.00 ps       |
  |   Vbias prefactor (k)  :  0.0600 Eh       |
  |   Vbias exponent (alpha)   :  0.7800 bohr-2   |
*MTD  11 completed successfully ...        0 min, 20.067 sec
*MTD   8 completed successfully ...        0 min, 13.054 sec
*MTD   4 completed successfully ...        0 min, 12.633 sec


 ====================================
 |  Multilevel Ensemble Optimization  |
 ====================================
 Optimizing all 686 structures from file "crest_dynamics.trj" ...
 ----------------------
 crude pre-optimization
 ----------------------
 Optimization engine: ANCOPT
 Hessian update type: BFGS
 E/G convergence criteria:  0.500E-03 Eh, 0.100E-01 Eh/a0
 maximum optimization steps: 200
 |>0.1% |>10.1% |>20.1% |>30.0% |>40.1% |>50.0% |>60.1% |>70.1% |>80.0% |>90.1% |>100.0%
```

```
 done.
> 686 of 686 structures successfully optimized (100.0% success)
> Total runtime for 686 optimizations:
 * wall-time:     0 d,  0 h,  0 min, 29.267 sec
 *  cpu-time:     0 d,  0 h,  1 min, 56.741 sec
 * ratio c/w:     3.989 speedup
> Corresponding to approximately 0.043 sec per processed structure

CREGEN> running RMSDs ... done.
CREGEN> E lowest :   -35.78090
 112 structures remain within    12.00 kcal/mol window
 ----------------------------------
 optimization with tight thresholds
 ----------------------------------
 Optimization engine: ANCOPT
 Hessian update type: BFGS
 E/G convergence criteria:  0.100E-05 Eh, 0.800E-03 Eh/a0
 maximum optimization steps: 200
 |>0.9% |>10.7% |>20.5% |>30.4% |>40.2% |>50.0% |>60.7% |>70.5% |>80.4% |>90.2% |>100.0%
 done.
> 112 of 112 structures successfully optimized (100.0% success)
> Total runtime for 112 optimizations:
 * wall-time:     0 d,  0 h,  0 min, 23.834 sec
 *  cpu-time:     0 d,  0 h,  1 min, 30.780 sec
 * ratio c/w:     3.809 speedup
> Corresponding to approximately 0.213 sec per processed structure
```

```
CREGEN> running RMSDs ... done.
CREGEN> E lowest :   -35.78144
 16 structures remain within     6.00 kcal/mol window


========================================
           MTD Simulations done
========================================
 Collecting ensmbles.
CREGEN> running RMSDs ... done.
CREGEN> E lowest :   -35.78144
 23 structures remain within     6.00 kcal/mol window



 ================================================
 Additional regular MDs on lowest 4 conformer(s)
 ================================================
  :::::::::::::: starting MD   1 ::::::::::::::
  |   MD simulation time   :     2.5 ps       |
  |   target T             :   400.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  :::::::::::::: starting MD   3 ::::::::::::::
  |   MD simulation time   :     2.5 ps       |
  |   target T             :   400.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
```

```
  |   SHAKE algorithm      : true (all bonds) |
  :::::::::::::: starting MD   2 ::::::::::::::
  |   MD simulation time   :     2.5 ps       |
  |   target T             :   400.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
  :::::::::::::: starting MD   8 ::::::::::::::
  |   MD simulation time   :     2.5 ps       |
  |   target T             :   500.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
*MD   1 completed successfully ...        0 min,  8.699 sec
  :::::::::::::: starting MD   4 ::::::::::::::
  |   MD simulation time   :     2.5 ps       |
  |   target T             :   400.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
*MD   3 completed successfully ...        0 min,  8.755 sec
  :::::::::::::: starting MD   5 ::::::::::::::
  |   MD simulation time   :     2.5 ps       |
  |   target T             :   500.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
```

```
*MD   2 completed successfully ...        0 min,  8.816 sec
  :::::::::::::: starting MD   6 ::::::::::::::
  |   MD simulation time   :     2.5 ps       |
  |   target T             :   500.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
*MD   8 completed successfully ...        0 min,  8.892 sec
  :::::::::::::: starting MD   7 ::::::::::::::
  |   MD simulation time   :     2.5 ps       |
  |   target T             :   500.0 K        |
  |   timestep dt          :     5.0 fs       |
  |   dump interval(trj)   :   100.0 fs       |
  |   SHAKE algorithm      : true (all bonds) |
*MD   6 completed successfully ...        0 min,  9.010 sec
*MD   5 completed successfully ...        0 min,  9.222 sec
*MD   7 completed successfully ...        0 min,  9.158 sec
*MD   4 completed successfully ...        0 min,  9.551 sec
 Appending file crest_rotamers_1.xyz with new structures
 Optimizing all 215 structures from file "crest_rotamers_1.xyz" ...
 ----------------------------------
 optimization with tight thresholds
 ----------------------------------
 Optimization engine: ANCOPT
 Hessian update type: BFGS
 E/G convergence criteria:  0.100E-05 Eh, 0.800E-03 Eh/a0
 maximum optimization steps: 200
```

```
 |>0.5% |>10.2% |>20.0% |>30.2% |>40.0% |>50.2% |>60.0% |>70.2% |>80.0% |>90.2% |>100.0%
 done.
> 215 of 215 structures successfully optimized (100.0% success)
> Total runtime for 215 optimizations:
 * wall-time:     0 d,  0 h,  0 min, 32.876 sec
 *  cpu-time:     0 d,  0 h,  2 min, 11.038 sec
 * ratio c/w:     3.986 speedup
> Corresponding to approximately 0.153 sec per processed structure

CREGEN> running RMSDs ... done.
CREGEN> E lowest :   -35.78144
 28 structures remain within     6.00 kcal/mol window


     ========================================
     |        Structure Crossing (GC)       |
     ========================================


 ============================
  # threads =           4
 ============================
input  file name : crest_rotamers_2.xyz
number of atoms                :      20
number of points on xyz files  :      28
conformer energy window  /kcal :    6.00
CN per atom difference cut-off :  0.3000
RMSD threshold (Ang, Bohr)     :  0.2500  0.4724
max. # of generated structures :      250
```

```
# in E window          28
 10.1 % done
 39.9 % done
 65.9 % done
 85.7 % done
100.0 % done
finished.
average rmsd w.r.t input     :     2.23629
number of clash discarded    :          15
removed identical structures :          57

250 structures written to confcross.xyz



=====================================
|  Multilevel Ensemble Optimization  |
=====================================
Optimizing all 250 structures from file "confcross.xyz" ...
----------------------
crude pre-optimization
----------------------
Optimization engine: ANCOPT
Hessian update type: BFGS
E/G convergence criteria:  0.500E-03 Eh, 0.100E-01 Eh/a0
maximum optimization steps: 200
|>0.4% |>10.0% |>20.0% |>30.0% |>40.0% |>50.0% |>60.0% |>70.4% |>80.0% |>90.4% |>100.0%
done.
```

```
> 250 of 250 structures successfully optimized (100.0% success)
> Total runtime for 250 optimizations:
 * wall-time:     0 d,  0 h,  0 min,  5.099 sec
 *  cpu-time:     0 d,  0 h,  0 min, 20.286 sec
 * ratio c/w:     3.979 speedup
> Corresponding to approximately 0.020 sec per processed structure

CREGEN> running RMSDs ... done.
CREGEN> E lowest :   -35.78144
 203 structures remain within    12.00 kcal/mol window
 ----------------------------------
 optimization with tight thresholds
 ----------------------------------
 Optimization engine: ANCOPT
 Hessian update type: BFGS
 E/G convergence criteria:  0.100E-05 Eh, 0.800E-03 Eh/a0
 maximum optimization steps: 200
 |>0.5% |>10.3% |>20.2% |>30.0% |>40.4% |>50.2% |>60.1% |>70.4% |>80.3% |>90.1% |>100.0%
 done.
> 203 of 203 structures successfully optimized (100.0% success)
> Total runtime for 203 optimizations:
 * wall-time:     0 d,  0 h,  0 min, 27.265 sec
 *  cpu-time:     0 d,  0 h,  1 min, 47.974 sec
 * ratio c/w:     3.960 speedup
> Corresponding to approximately 0.134 sec per processed structure

CREGEN> running RMSDs ... done.
```

```
CREGEN> E lowest :   -35.78144
 76 structures remain within     6.00 kcal/mol window
appending new structures to crest_rotamers_2.xyz
CREGEN> running RMSDs ... done.
CREGEN> E lowest :   -35.78144



   ================================================
   |           Final Geometry Optimization        |
   ================================================
 Optimizing all 79 structures from file "crest_rotamers_3.xyz" ...
 ----------------------------------------
 optimization with very tight thresholds
 ----------------------------------------
 Optimization engine: ANCOPT
 Hessian update type: BFGS
 E/G convergence criteria:  0.100E-06 Eh, 0.200E-03 Eh/a0
 maximum optimization steps: 200
 |>1.3% |>10.1% |>20.3% |>30.4% |>40.5% |>50.6% |>60.8% |>70.9% |>81.0% |>91.1% |>100.0%
 done.
> 79 of 79 structures successfully optimized (100.0% success)
> Total runtime for 79 optimizations:
 * wall-time:     0 d,  0 h,  0 min,  4.520 sec
 *  cpu-time:     0 d,  0 h,  0 min, 17.910 sec
 * ratio c/w:     3.962 speedup
> Corresponding to approximately 0.057 sec per processed structure
```

```
CREGEN> running RMSDs ... done.
CREGEN> E lowest :   -35.78144
 70 structures remain within     6.00 kcal/mol window



 -------------------------
 Final Ensemble Information
 -------------------------
 input  file name : crest_rotamers_3.xyz
 output file name : crest_rotamers_4.xyz
 number of atoms                :   20
 number of points on xyz files  :   79
 RMSD threshold                 :   0.1250
 Bconst threshold               :   0.0100
 population threshold           :   0.0500
 # fragment in coord            :    2
 # bonds in reference structure :    18
 number of reliable points      :    79
 sorting energy window (EWIN)   :    6.0000 / kcal*mol-1
 reference state Etot           :  -35.781440510000003
 number of doubles removed by rot/RMSD         :           9
 total number unique points considered further :          70
       Erel/kcal        Etot weight/tot  conformer     set   degen     origin
       1   0.000   -35.78144    0.14300    0.28600       1       2
       2   0.000   -35.78144    0.14300
       3   0.547   -35.78057    0.07998    0.31991       2       4
       4   0.547   -35.78057    0.07998
```

5	0.547	-35.78057	0.07998			
6	0.547	-35.78057	0.07997			
7	0.981	-35.77988	0.05044	0.10088	3	2
8	0.981	-35.77988	0.05044			
9	2.219	-35.77790	0.01353	0.09473	4	7
10	2.219	-35.77790	0.01353			
11	2.219	-35.77790	0.01353			
12	2.219	-35.77790	0.01353			
13	2.219	-35.77790	0.01353			
14	2.219	-35.77790	0.01353			
15	2.219	-35.77790	0.01353			
16	2.253	-35.77785	0.01304	0.01304	5	1
17	2.729	-35.77709	0.00787	0.11677	6	15
18	2.729	-35.77709	0.00787			
19	2.729	-35.77709	0.00787			
20	2.729	-35.77709	0.00787			
21	2.729	-35.77709	0.00787			
22	2.730	-35.77709	0.00786			
23	2.730	-35.77709	0.00786			
24	2.747	-35.77706	0.00772			
25	2.747	-35.77706	0.00772			
26	2.748	-35.77706	0.00772			
27	2.748	-35.77706	0.00772			
28	2.748	-35.77706	0.00772			
29	2.748	-35.77706	0.00771			
30	2.748	-35.77706	0.00771			
31	2.749	-35.77706	0.00771			

32	3.197	-35.77635	0.00479	0.03829	7	8
33	3.197	-35.77635	0.00479			
34	3.197	-35.77635	0.00479			
35	3.197	-35.77635	0.00479			
36	3.197	-35.77635	0.00479			
37	3.197	-35.77635	0.00479			
38	3.197	-35.77635	0.00478			
39	3.198	-35.77634	0.00478			
40	3.472	-35.77591	0.00357	0.00357	8	1
41	3.995	-35.77507	0.00205	0.00205	9	1
42	4.404	-35.77442	0.00133	0.00265	10	2
43	4.407	-35.77442	0.00132			
44	4.437	-35.77437	0.00128	0.00512	11	4
45	4.437	-35.77437	0.00128			
46	4.437	-35.77437	0.00128			
47	4.437	-35.77437	0.00128			
48	4.511	-35.77425	0.00118	0.00474	12	4
49	4.511	-35.77425	0.00118			
50	4.511	-35.77425	0.00118			
51	4.511	-35.77425	0.00118			
52	4.826	-35.77375	0.00085	0.00085	13	1
53	4.941	-35.77357	0.00075	0.00450	14	6
54	4.941	-35.77357	0.00075			
55	4.942	-35.77357	0.00075			
56	4.942	-35.77357	0.00075			
57	4.942	-35.77357	0.00075			
58	4.942	-35.77357	0.00075			

```
      59   5.033   -35.77342    0.00068    0.00476      15       7
      60   5.033   -35.77342    0.00068
      61   5.033   -35.77342    0.00068
      62   5.033   -35.77342    0.00068
      63   5.033   -35.77342    0.00068
      64   5.034   -35.77342    0.00068
      65   5.034   -35.77342    0.00068
      66   5.426   -35.77279    0.00045    0.00090      16       2
      67   5.427   -35.77279    0.00045
      68   5.508   -35.77266    0.00041    0.00123      17       3
      69   5.508   -35.77266    0.00041
      70   5.508   -35.77266    0.00041
T /K                                  :   473.15
E lowest                              :   -35.78144
ensemble average energy (kcal)        :    1.094
ensemble entropy (J/mol K, cal/mol K) :   25.837    6.175
ensemble free energy (kcal/mol)       :   -2.922
population of lowest in %             :   28.600
 number of unique conformers for further calc           17
 list of relative energies saved as "crest.energies"

 -----------------
 Wall Time Summary
 -----------------
 CREST runtime (total)                0 d,  0 h,  5 min, 12.552 sec
 ----------------------------------------------------------------------
 Trial metadynamics (MTD)   ...        0 min,  2.301 sec (  0.736%)
```

```
Metadynamics (MTD)         ...        2 min,  7.401 sec ( 40.761%)
Geometry optimization      ...        2 min, 11.661 sec ( 42.125%)
Molecular dynamics (MD)    ...        0 min, 18.258 sec (  5.842%)
Genetic crossing (GC)      ...        0 min, 32.761 sec ( 10.482%)
I/O and setup              ...        0 min,  0.170 sec (  0.054%)
-------------------------------------------------------------------
* wall-time:     0 d,  0 h,  5 min, 12.552 sec
*  cpu-time:     0 d,  0 h, 19 min, 28.550 sec
* ratio c/w:     3.739 speedup
-------------------------------------------------------------------
* Total number of energy+grad calls: 73605

CREST terminated normally.
```

3 Electronic and zero-point corrected relative energies

Table S1: Relative energies and enthalpies at 0 K (in eV) using the B3 level of theory. Energies correspond to molecular species at each critical point treated as non-covalently bound complexes. Values in parentheses refer to the corresponding energies for fully separated species, while values in square brackets are in kcal mol^{-1}.

	ΔE	$\Delta H_{0\,\mathrm{K}}$
$2C_2H_5NO_2$	0.00 (0.00) [0.00 (0.00)]	0.00 (0.00) [0.00 (0.00)]
$C_2H_5NO_2 \ldots C_2H_5NO_2$	-0.80 (-0.80) [-18.44 (-18.44)]	-0.75 (-0.75) [-17.29 (-17.29)]
GlyGly + H_2O	-0.74 (-0.24) [-17.05 (-5.53)]	-0.67 (-0.27) [-15.44 (-6.22)]
Anhy + H_2O	0.19 (0.66) [4.38 (15.23)]	0.18 (0.56) [4.15 (12.94)]
Int-N	0.01 (0.01) [0.23 (0.23)]	0.14 (0.14) [3.22 (3.22)]
Int-O	0.14 (0.14) [3.22 (3.22)]	0.23 (0.23) [5.29 (5.29)]
Int−1 + H_2O	-0.02 (-) [-0.46 (-)]	0.01 (-) [0.23 (-)]
Int−2 + H_2O + CO	1.12 (-) [25.82 (-)]	0.92 (-) [21.19 (-)]
Int−3 + H_2O	-0.16 (0.40) [-3.69 (9.22)]	-0.05 (0.39) [-1.15 (8.99)]
Int−4 + 2 H_2O	-0.95 (0.13) [-21.88 (3.00)]	-0.93 (-0.06) [-21.42 (-1.38)]
Int−5 + 2 H_2O	-0.53 (0.61) [-12.21 (14.08)]	-0.53 (0.41) [-12.21 (9.48)]
Int−6 + 2 H_2O	-0.10 (1.03) [-2.30 (23.82)]	-0.10 (0.82) [-2.30 (19.06)]
Int−7 + H_2O	0.41 (0.94) [9.43 (21.72)]	0.44 (0.87) [10.11 (20.12)]
Int−8 + 2 H_2O	0.41 (1.43) [9.43 (33.03)]	0.40 (1.20) [9.19 (27.69)]
Int−9 + H_2O	-0.03 (0.45) [-0.69 (10.39)]	0.06 (0.43) [1.38 (9.91)]
Int−10 + 2 H_2O	0.13 (1.03) [3.00 (23.82)]	0.10 (0.80) [2.30 (18.38)]
Int−11 + NH_3	-0.48 (0.12) [-11.07 (2.76)]	-0.46 (0.06) [-10.61 (1.38)]
Int−13 + 2 NH_3	0.19 (0.90) [4.38 (20.64)]	0.17 (0.73) [3.92 (16.74)]
Int−14 + H_2O + NH_3	-0.50 (0.52) [-11.53 (11.93)]	-0.50 (0.34) [-11.53 (7.78)]
TS-GG	1.34 (1.34) [30.86 (30.86)]	1.32 (1.32) [30.37 (30.37)]
TS-Anhy	1.03 (1.03) [23.72 (23.72)]	0.98 (0.98) [22.56 (22.56)]
TS-N	1.47 (1.47) [33.91 (33.91)]	1.46 (1.46) [33.67 (33.67)]
TS-O	0.48 (0.48) [11.08 (11.08)]	0.49 (0.49) [11.32 (11.32)]
TS-N-GG	1.27 (1.27) [29.27 (29.27)]	1.24 (1.24) [28.58 (28.58)]
TS-O-Anhy	2.01 (2.01) [46.36 (46.36)]	1.94 (1.94) [44.74 (44.74)]
TS−GG−1 + H_2O	1.37 (-) [31.57 (-)]	1.27
TS−GG−3 + H_2O	1.21 (1.81) [27.86 (41.65)]	1.18 (1.66) [27.14 (38.15)]
TS−GG−7 + H_2O	2.13 (2.68) [48.99 (61.66)]	2.02 (2.44) [46.41 (56.18)]
TS−GG−14 + H_2O	2.27 (1.81) [52.19 (41.65)]	2.20 (1.72) [50.56 (39.57)]
TS−Anhy−9 + H_2O	1.38 (2.02) [31.73 (46.57)]	1.34 (1.87) [30.86 (43.08)]
TS−1-2 + H_2O	2.22 (-) [51.02 (-)]	2.10 (-) [48.26 (-)]
TS−3-4 + H_2O	0.96 (1.69) [22.06 (38.81)]	0.93 (1.51) [21.38 (34.67)]
TS−4-5 + 2 H_2O	1.00 (2.09) [22.99 (47.97)]	0.88 (1.76) [20.23 (40.40)]
TS−5-6 + 2 H_2O	1.40 (2.53) [32.18 (58.08)]	1.27 (2.19) [29.27 (50.34)]
TS−7-8 + H_2O	2.37 (2.93) [54.50 (67.05)]	2.30 (2.72) [52.87 (62.23)]
TS−9-8 + H_2O	2.29 (2.58) [52.67 (58.82)]	2.02 (2.21) [46.41 (50.41)]
TS−9-10 + H_2O	1.79 (2.54) [41.18 (57.84)]	1.75 (2.41) [40.24 (55.00)]
TS−11-13 + NH_3	3.06 (3.33) [70.43 (76.68)]	2.96 (3.17) [68.12 (72.82)]
TS-VdW-11	2.65 (2.65) [60.99 (60.99)]	2.61 (2.61) [60.07 (60.07)]
Int-IC	-1.70 (-) [-39.20 (-)]	-1.52 (-) [-35.05 (-)]
Int−11 + NH_3	-1.63 (-) [-37.56 (-)]	-1.49 (-) [-34.29 (-)]
Int−12 + NH_3	-1.70 (-) [-39.20 (-)]	-1.50 (-) [-34.54 (-)]
Int−13 + 2 NH_3	-1.06 (-) [-24.44 (-)]	-0.94 (-) [-21.65 (-)]
GlyGly−Z + H_2O	-2.22 (-) [-51.33 (-)]	-2.01 (-) [-46.51 (-)]
Int−14 + H_2O + NH_3	-1.49 (-) [-34.47 (-)]	-1.37 (-) [-31.73 (-)]
TS-IC-11	-0.05 (-) [-1.15 (-)]	0.07 (-) [1.61 (-)]
TS−12-13 + NH_3	0.29 (-) [6.68 (-)]	0.36 (-) [8.29 (-)]
TS−GGZ−14 + H_2O	-0.47 (-) [-10.86 (-)]	-0.32 (-) [-7.40 (-)]
GlyGly−Z + H_2O	-2.90 (-) [-67.17 (-)]	-2.61 (-) [-60.44 (-)]
Trimer−1 + H_2O + NH_3	-2.79 (-) [-64.59 (-)]	-2.53 (-) [-58.54 (-)]
Int−12 + NH_3	-2.53 (-) [-58.54 (-)]	-2.25 (-) [-52.04 (-)]
Trimer−2 + 2 NH_3	-2.38 (-) [-55.07 (-)]	-2.18 (-) [-50.38 (-)]
TS−GGZ−Trimer1 + H_2O	-1.75 (-) [-40.50 (-)]	-1.49 (-) [-34.47 (-)]
TS−12-Trimer2 + NH_3	-1.41 (-) [-32.62 (-)]	-1.18 (-) [-27.29 (-)]

4 Electronic, zero-point corrected and free energies barriers

Table S2: Barrier heights (in eV) calculated at 0 K and 473.15 K using the B3 level of theory. Barriers correspond to molecular species treated as non-covalently bound complexes. Values in parentheses refer to the corresponding energies for fully separated species, while values in square brackets are in kcal mol^{-1}.

	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}_{0\,\mathrm{K}}$	$\Delta G^{\ddagger}_{473.15\,\mathrm{K}}$
$C_2H_5NO_2 \ldots C_2H_5NO_2 \longleftrightarrow$ GlyGly + H_2O	2.14/2.08 [49.35/47.97]	2.07/1.99 [47.77/45.89]	2.18/2.07 [50.26/47.97]
	(2.14/1.58 [49.35/36.45])	(2.07/1.60 [47.77/36.90])	(2.18/2.36 [50.26/54.41])
$C_2H_5NO_2 \ldots C_2H_5NO_2 \longleftrightarrow$ Int−N	2.21/1.46 [50.97/33.67]	2.13/1.32 [49.14/30.45]	2.22/1.31 [51.20/30.22]
	(1.71/1.46 [39.43/33.67])	(1.73/1.32 [39.89/30.45])	(2.51/1.31 [57.87/30.22])
Int−N $\longleftrightarrow$ GlyGly	1.26/2.01 [29.06/46.31]	1.10/1.91 [25.37/44.04]	1.08/1.99 [24.91/45.89]
	(1.26/1.50 [29.06/34.59])	(1.10/1.51 [25.37/34.82])	(1.08/2.28 [24.91/52.60])
$C_2H_5NO_2 \ldots C_2H_5NO_2 \longleftrightarrow$ Anhy + H_2O	1.84/0.84 [42.43/19.37]	1.74/0.80 [40.13/18.45]	1.79/0.91 [41.29/20.99]
	(1.84/0.37 [42.43/8.53])	(1.74/0.43 [40.13/9.91])	(1.79/1.21 [41.29/27.91])
$C_2H_5NO_2 \ldots C_2H_5NO_2 \longleftrightarrow$ Int−O	1.29/0.35 [29.74/8.07]	1.24/0.25 [28.60/5.77]	1.34/0.26 [30.89/5.99]
	(1.29/0.35 [29.74/8.07])	(1.24/0.25 [28.60/5.77])	(1.34/0.26 [30.89/5.99])
Int−O $\longleftrightarrow$ Anhy	1.88/1.83 [43.39/42.24]	1.71/1.77 [39.43/40.63]	1.71/1.90 [39.43/43.82]
	(1.88/1.35 [43.39/31.13])	(1.71/1.39 [39.43/32.05])	(1.71/2.20 [39.43/50.73])
GlyGly $\longleftrightarrow$ Int−1	2.11/1.39 [48.67/32.05]	1.94/1.26 [44.74/29.06]	1.93/1.27 [44.51/29.29]
	(2.13/1.38 [49.14/31.82])	(1.97/1.25 [45.43/28.83])	(1.97/1.26 [45.43/29.06])
Int−1 $\longleftrightarrow$ Int−2 + H_2O + CO	2.24/1.10 [51.67/25.37]	2.09/1.18 [48.21/27.22]	2.03/1.38 [46.84/31.82]
	(-)	(-)	(-)
GlyGly $\longleftrightarrow$ Int−3	1.95/1.36 [44.97/31.36]	1.85/1.23 [42.67/28.34]	1.95/1.25 [44.97/28.83]
	(2.04/1.41 [47.06/32.53])	(1.94/1.28 [44.74/29.52])	(2.03/1.30 [46.84/29.98])
Int−3 $\longleftrightarrow$ Int−4 + H_2O	1.12/1.92 [25.83/44.27]	0.98/1.86 [22.60/42.84]	0.96/1.97 [22.14/45.45]
	(1.29/1.56 [29.74/35.97])	(1.12/1.57 [25.83/36.21])	(1.11/2.34 [25.60/53.93])
Int−4 $\longleftrightarrow$ Int−5	1.95/1.53 [44.97/35.26]	1.81/1.40 [41.73/32.29]	1.83/1.40 [42.20/32.29]
	(1.97/1.49 [45.43/34.37])	(1.82/1.35 [41.97/31.13])	(1.84/1.36 [42.43/31.36])
Int−5 $\longleftrightarrow$ Int−6	1.93/1.50 [44.51/34.59]	1.79/1.37 [41.29/31.59]	1.82/1.38 [41.97/31.82]
	(1.92/1.50 [44.28/34.59])	(1.78/1.37 [41.06/31.59])	(1.80/1.37 [41.52/31.59])
GlyGly $\longleftrightarrow$ Int−7	2.87/1.72 [66.18/39.67]	2.69/1.57 [62.06/36.21]	2.69/1.59 [62.06/36.67]
	(2.92/1.74 [67.33/40.13])	(2.72/1.57 [62.75/36.21])	(2.70/1.55 [62.29/35.75])
Int−7 $\longleftrightarrow$ Int−8 + H_2O	1.96/1.96 [45.20/45.20]	1.86/1.90 [42.90/43.82]	1.91/2.00 [44.04/46.12]
	(1.99/1.50 [45.89/34.59])	(1.85/1.52 [42.67/35.05])	(1.89/2.29 [43.58/52.83])
Int−9 $\longleftrightarrow$ Int−8 + H_2O	2.32/1.88 [53.69/43.39]	1.96/1.63 [45.20/37.63]	1.84/1.63 [42.67/37.63]
	(2.09/1.11 [48.21/25.60])	(1.78/1.01 [41.06/23.29])	(1.74/1.76 [40.13/40.51])
GlyGly $\longleftrightarrow$ Int−14 + NH_3	3.01/2.77 [69.58/63.88]	2.87/2.70 [66.18/62.26]	2.85/2.74 [65.72/63.18]
	(2.05/1.29 [47.29/29.74])	(1.99/1.38 [45.89/31.82])	(2.02/2.09 [46.60/48.21])
Anhy $\longleftrightarrow$ Int−9	1.19/1.41 [27.44/32.53]	1.16/1.28 [26.75/29.52]	1.33/1.29 [30.66/29.74]
	(1.36/1.58 [31.36/36.45])	(1.32/1.45 [30.45/33.44])	(1.46/1.46 [33.67/33.67])
Int−9 $\longleftrightarrow$ Int−10 + H_2O	1.82/1.67 [41.06/38.33]	1.69/1.65 [38.99/38.10]	1.67/1.79 [38.53/41.29]
	(2.13/1.55 [49.14/35.74])	(1.99/1.61 [45.89/37.11])	(1.96/2.37 [45.20/54.84])
$C_2H_5NO_2 \ldots C_2H_5NO_2 \longleftrightarrow$ Int−11 + NH_3	3.45/3.13 [79.61/72.17]	3.36/3.07 [77.48/70.92]	3.38/3.11 [77.94/71.85]
	(3.45/2.52 [79.61/58.12])	(3.36/2.54 [77.48/58.59])	(3.65/3.49 [84.21/80.51])
Int−11 $\longleftrightarrow$ Int−13 + NH_3	3.54/2.87 [81.82/66.18]	3.42/2.79 [78.64/64.32]	3.38/2.80 [77.94/64.55]
	(3.21/2.43 [73.99/56.05])	(3.10/2.43 [71.49/56.05])	(3.11/3.09 [71.73/71.26])
Int−IC $\longleftrightarrow$ Int−11	1.65/1.59 [38.05/36.67]	1.60/1.56 [36.90/36.05]	1.61/1.61 [37.13/37.13]
	(-)	(-)	(-)
Int−12 $\longleftrightarrow$ Int−13	1.98/1.35 [45.66/31.13]	1.86/1.30 [42.90/29.98]	1.72/1.32 [39.66/30.45]
	(-)	(-)	(-)
GlyGly−Z $\longleftrightarrow$ Int−14	1.76/1.02 [40.58/23.51]	1.69/1.05 [38.99/24.22]	1.61/1.14 [37.13/26.29]
	(-)	(-)	(-)
GlyGly−Z $\longleftrightarrow$ Trimer−1	1.15/1.04 [26.51/23.98]	1.12/1.05 [25.83/24.21]	1.18/1.18 [27.21/27.21]
	(-)	(-)	(-)
Int−12 $\longleftrightarrow$ Trimer−2	1.12/0.97 [25.83/22.37]	1.07/1.00 [24.68/23.06]	1.06/1.10 [24.45/25.37]
	(-)	(-)	(-)