Dimerisation of Nitrile Oxides: a Quantum-chemical Study

Supplementary Information

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Table S1: Total and relative energies of selected fluoro derivatives

<table>
<thead>
<tr>
<th></th>
<th>MRCI(2,2)</th>
<th>MRCI(2,2)+DA</th>
<th>MR-AQCC(2,2)</th>
<th>MRCI(4,4)</th>
<th>MRCI(4,4)+DA</th>
<th>MR-AQCC(4,4)</th>
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<tr>
<td></td>
<td>Total energy</td>
<td>ΔG</td>
<td>Total energy</td>
<td>ΔG</td>
<td>Total energy</td>
<td>ΔG</td>
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<td>2 FCNO</td>
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<td>2(-267.280205)</td>
<td>119</td>
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<td>.571730</td>
<td>-5</td>
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<tr>
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<td>.564997</td>
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<td>.615065</td>
<td>-105</td>
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<td>-92</td>
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a Total energies are in atomic units and relative Gibbs energies are in kJ/mol. Calculated using the 6-311+G(2d) basis set. Geometries, ZPE, and thermal corrections are calculated at the UB3LYP/6-311+G(d) level. Valence electrons were included in the correlation energy calculations (“fc”).
Table S2: Total energies (in atomic units) of the minima and transition states of the lowest energy TS5 dimerisation routes of Nitrile Oxides to Furoxans\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>FCNO</th>
<th>CICNO</th>
<th>BrCNO</th>
<th>CH\textsubscript{3}CNO</th>
<th>NCCNO</th>
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<tr>
<td>XCNO</td>
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<td>-627.3833</td>
<td>-2740.3079</td>
<td>-207.5258</td>
<td>-260.34694</td>
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<tr>
<td>TS1</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
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<tr>
<td>ctc</td>
<td>-534.80422</td>
<td>-1254.8041</td>
<td>-5480.6332</td>
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<tr>
<td>TS2</td>
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\textsuperscript{a} Calculated at the MR-AQCC(2,2)//UB3LYP/cc-pVTZ level. Total energies of monomers are calculated at the SR-AQCC//B3LYP/cc-pVTZ level.

Table S3: Total energies (in atomic units) of the minima and transition states of the dimerisation routes of Nitrile Oxides to 1,2,4-oxadiazole-4-oxides (SP1) and 1,4,2,5-dioxadiazines (SP2)\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>FCNO</th>
<th>ClCNO</th>
<th>BrCNO</th>
<th>CH\textsubscript{3}CNO</th>
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<td>SP1</td>
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<td>-415.1487</td>
<td>-520.77215</td>
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\textsuperscript{a} Calculated at the CCSD//B3LYP/cc-pVTZ and CCSD(T)//B3LYP/cc-pVTZ (in parenthesis) levels.

Table S4: Total energies (in atomic units) of the NCCNO dimers and trimers\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
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<th>Trimmers</th>
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<tr>
<td></td>
<td>TSdm1</td>
<td>TStr1</td>
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<tr>
<td></td>
<td>DM1</td>
<td>TStr1\textsuperscript{b}</td>
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<tr>
<td></td>
<td>TSDm2</td>
<td>TR1</td>
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<tr>
<td></td>
<td>DM2</td>
<td>TStr2,3\textsuperscript{b}</td>
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<tr>
<td></td>
<td>TS1\textsuperscript{b}</td>
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<tr>
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<td>TStr3</td>
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</tr>
</tbody>
</table>

\textsuperscript{a} Calculated at the CCSD//B3LYP/cc-pVTZ level.
\textsuperscript{b} Calculated at the MR-AQCC(2,2)//UB3LYP/cc-pVTZ level.
Figure S1
Dimerisation of FCNO

MR-AQCC(2,2)/6-311+G(2d)//UB3LYP/6-311+G(d)
UB3LYP/6-311+G(d)

Supplementary Material (ESI) for PCCP
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Figure S2

Geometries (bond lengths in Å and bond angles in degrees) and bond orders (circled numbers) of minima on the potential energy surface for FCNO dimerisation (UB3LYP/cc-pVTZ).
Geometries (bond lengths in Å and bond angles in degrees) and bond orders (circled numbers) of minima on the potential energy surface for BrCNO dimerisation (UB3LYP/cc-pVTZ).

**Figure S3**

Supplementary Material (ESI) for PCCP

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**Geometries (bond lengths in Å and bond angles in degrees) and bond orders (circled numbers) of minima on the potential energy surface for CH$_3$CNO dimerisation (UB3LYP/cc-pVTZ).**

**Figure S4**
Geometries (bond lengths in Å and bond angles in degrees) and bond orders (circled numbers) of minima on the potential energy surface for NCCNO dimerisation (UB3LYP/cc-pVTZ).

Figure S5
Geometries (bond lengths in Å and bond angles in degrees) and bond orders (circled numbers) of 1,2,4-oxadiazole-4-oxides, SP1 (B3LYP/cc-pVTZ).

Figure S6
Figure S7

Geometries (bond lengths in Å and bond angles in degrees) and bond orders (circled numbers) of 1,4,2,5-dioxadiazines, SP2 (B3LYP/cc-pVTZ).
Geometries (bond lengths in Å and bond angles in degrees) and bond orders (circled numbers) of NCCNO dimers and trimers (B3LYP/cc-pVTZ).

Figure S8