Supplementary Material

Rearrangement and cyclisation reactions on the 1-arylpurrol-2-iminy – 2-arylaminopyrrol-1-yl radical energy surface

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Experimental

1-(p-Tolyl)pyrrole 6.

A mixture of p-toluidine (4.53 g, 42.3 mmol), 2,5-dimethoxycyclohexa-2,4-diene (6.01 g, 45 mmol) and glacial acetic acid (20 cm³) was heated under reflux for 2 h. The volatiles were removed under reduced pressure, water (100 cm³) was added and the reaction mixture extracted with dichloromethane (3 × 80 cm³). The combined organic extracts were washed with water (80 cm³), dried (MgSO₄) and concentrated to give crude 6 (5.71 g, 86%), mp 77-78 °C (lit.¹ 81-82 °C) δH 7.30-7.19 (4H, m), 7.06 (2H, t, 3J 2.2), 6.33 (2H, t, 3J 2.2) and 2.37 (3H, s); δC 138.32 (quat), 135.22 (quat), 129.89, 120.39, 119.24, 109.90 and 20.72; m/z 157 (M⁺, 100%), 115 (39) and 91 (30).

1-(p-Tolyl)pyrrole-2-carbaldehyde 7

A solution of 1-p-tolylpyrrole 6 (4.023 g, 25.6 mmol) in DMF (40 cm³) was added to a solution of phosphoryl chloride (5.19 g, 33.2 mmol) in DMF (85 cm³) and stirred for 1 h. A further portion of phosphoryl chloride (5.19 g, 33.2 mmol) in DMF (85 cm³) was added and stirring continued for another hour. The reaction mixture was poured onto crushed ice, hydrolysed with dilute aqueous sodium hydroxide (2 M, 200 cm³) and acidified to pH 6-7 with dilute hydrochloric acid (2 M, 20 cm³). The mixture was then extracted with ether (3 × 250 cm³) and the combined organic extracts were washed with water (200 cm³) and dried (MgSO₄). The solvent was removed under reduced pressure to give crude aldehyde as an orange oil. Distillation removed remaining traces of DMF and the aldehyde crystallised as an orange solid. TLC showed that formylation had occurred at both the 2 and 3-positions and so the mixture was recrystallised from light petroleum (bp 40-60 °C) to yield only the 2-isomer 7 as white crystals (3.30 g, 70%), mp 54-56 °C (lit.,² 55 °C); δH 9.55 (1H, s), 7.25-7.23 (4H, m), 7.15-7.13 (2H, m), 7.05-7.03 (2H, m), 6.38 (1H, m) and 2.41 (3H, s) (spectrum consistent with literature data³); δC 178.99, 138.11 (quat), 136.08 (quat), 132.46 (quat), 130.90, 129.55, 125.71, 121.54, 110.56 and 21.00; m/z 185 (M⁺, 100%), 157 (55), 128 (36) and 92 (83).

N,N-(Dimethylamino)pyrrole 9

2,5-Dimethoxycyclohexa-2,4-diene (11 g, 83 mmol) was added to a stirred solution of N,N-dimethylhydrazine (5 g, 83 mmol) in acetic acid (15 cm³) and heated at reflux for 2.5 h. The mixture was then quenched with sodium bicarbonate solution and extracted with dichloromethane (100 cm³); the organic layer was washed with water (2 × 50 cm³) and then brine (50 cm³). The organic layer was then dried (MgSO₄) filtered and concentrated under vacuum. The residue was purified by distillation, bp 100-105 °C (15 Torr) [lit.,⁴ 138-140 °C (767 Torr)], to give 9 as a pale yellow oil (4.9 g, 54%); δH 6.90 (2H, d, 3J 2.2), 6.08 (2H, 3J 2.2) and 2.87 (6H, s); δC 116.20 (2CH), 105.67 (2CH) and 48.27 (2CH₃).

FVP reactions

General conditions are given in the main paper.

FVP of N,N-(dimethylamino)pyrrole 9 – temperature profile

Due to its low boiling point (138-140 °C at atmospheric pressure) N,N-(dimethylamino)pyrrole 9 was frozen in the inlet system using an acetone/dry ice bath which remained in place around the inlet as the vacuum was applied. The cooling bath was then slowly removed allowing the N,N-(dimethylamino)pyrrole 9 to volatilise into the furnace tube in a controlled manner.

Tᵣ 550 °C, (24.8 mg, Tᵣ RT, P 2.3-2.4 × 10⁻² Torr, t 16 min) gave N,N-(dimethylamino)pyrrole 9 (ca 97%)
Tᵣ 600 °C, (21.5 mg, Tᵣ RT, P 2.4-3.0 × 10⁻² Torr, t 17 min) gave N,N-(dimethylamino)pyrrole 9 (ca 92%) and pyrrole 10 (ca 8%)
$T_t 650 \, ^\circ C$, (21.3 mg, $T_t$ RT, $P 2.6-3.5 \times 10^{-2}$ Torr, t 16 min) gave $N,N$-(dimethylamino)pyrrole 9 (ca 63%) and pyrrole 10 (ca 37%)

$T_t 700 \, ^\circ C$, (21.6 mg, $T_t$ RT, $P 2.6-3.2 \times 10^{-2}$ Torr, t 15 min) gave $N,N$-(dimethylamino)pyrrole 9 (ca 21%) and pyrrole 10 (ca 79%)

$T_t 750 \, ^\circ C$, (24.3 mg, $T_t$ RT, $P 2.8-5.0 \times 10^{-2}$ Torr, t 17 min) gave $N,N$-(dimethylamino)pyrrole 9 (ca 18%) and pyrrole 10 (ca 82%)

$T_t 800 \, ^\circ C$, (24.6 mg, $T_t$ RT, $P 2.5-6.0 \times 10^{-2}$ Torr, t 16 min) gave $N,N$-(dimethylamino)pyrrole 9 (ca 3%) and pyrrole 10 (ca 97%)

$T_t 850 \, ^\circ C$, (25.5 mg, $T_t$ RT, $P 3.2-7.3 \times 10^{-2}$ Torr, t 19 min) gave pyrrole 10 (ca 99%).

**N-(Dimethylamino)-3-(2-p-tolyvinyl)pyrrole 15**

Synthesised as described in the main paper for 13, from $N$-(dimethylamino)pyrrole-3-carboxaldehyde 14 in 60% yield, $N$-(dimethylamino)-3-(2-p-tolyvinyl)pyrrole 15 had mp 70 °C; (Found: M$^+$ 226.1469. C$_{15}$H$_{18}$N$_2$ requires M 226.1470); δ$_H$ 7.34 (2H, d, $^3$J 8.1), 7.13 (2H, d, $^3$J 8.1), 6.97 (1H, m), 6.94 (1H, d, $^3$J 16.5), 6.84 (1H, t, $^3$J 2.8), 6.75 (1H, d, $^3$J 16.5), 6.31 (1H, t, $^3$J 2.8), 2.85 (6H, s) and 2.65 (3H, s); δ$_C$ 135.98 (quat), 135.45 (quat), 129.10 (2CH), 125.51 (2CH), 124.17 (CH), 121.24 (CH), 120.52 (quat), 117.80 (CH), 115.62 (CH), 103.12 (CH), 48.20 (2CH$_3$) and 21.04 (CH$_3$); m/z 226 (M$^+$, 100%) and 167 (66).

**FVP of N,N-dimethylamino-3-(2-p-tolyvinyl)pyrrole 15**

FVP of $N,N$-dimethylamino-3-(2-p-tolyvinyl)pyrrole 15 [116 mg (0.51 mmol) $T_t$ 750 °C, $T_t$ 140 °C, $P 2.1-10^{-10}$ Torr, t 1 h] gave a mixture of products: 8-methylpyrrolo[1,2-a]quinoline 19 (4.6 mg, 5%); δ$_H$ 7.71 (1H, s), 7.54 (1H, d, $^3$J 7.9), 7.34 (1H, m), 7.27 (1H, d, $^3$J 9.3), 7.15 (1H, d, $^3$J 7.9), 6.97 (1H, d, $^3$J 9.3), 6.80 (1H, t, $^3$J 3.2), 6.52 (1H, m) and 2.56 (3H, s): 3-(2-p-tolyvinyl)pyrrole 20 (10.3 mg, 11%) (Found: M$^+$ 183.1047. C$_{13}$H$_{13}$N requires M 183.1048); δ$_H$ 8.16 (1H, br. s), 7.37 (2H, d, $^3$J 8.1), 7.15 (2H, d, $^3$J 8.1), 7.04 (1H, d, $^3$J 16.2), 6.90 (1H, dd, $^3$J 4.2), 6.81 (1H, d, $^3$J 16.2), 6.80 (1H, dd, $^4$J 2.6), 6.51 (1H, dd, $^3$J 4.2, $^4$J 2.6) and 2.36 (3H, s); δ$_C$ 136.04 (quat), 129.12 (2CH), 125.56 (2CH), 124.60 (CH), 123.10 (quat), 119.01 (CH), 117.12 (CH), 105.45 (CH) and 20.82 (CH$_3$) (spectra consistent with literature data$^3$); m/z 183 (M$^+$, 100%): a fraction which was tentatively identified as impure 8-methylbenzo[g]indole S1 (trace) (Found: M$^+$ 181.0891. C$_{13}$H$_{11}$N requires M 181.0892); δ$_H$ 9.01 (1H, br. s), 7.85-7.80 (2H, m), 7.67 (1H, d, $^3$J 8.5), 7.49 (1H, d, $^3$J 8.5), 7.36-7.13 (2H, m), 6.12 (1H, m) and 2.39 (3H, s); m/z 181 (M$^+$, 100%) and 84 (92).
Formation of products from FVP of \(N,N\)-dimethylamino-3-(2-p-tolylvinyl)pyrrole 15

![Scheme 9 (from main paper)](image)

Three products were isolated, in low yield, from FVP of 15. The product of hydrogen-capture by the pyrrol-1-yl radical, 20, retains the carbon skeleton of the precursor. Similarly, the formation of 8-methylbenzo[g]indole S1, tentatively identified in trace amounts from an impure fraction, is consistent with delocalisation of the pyrrol-1-yl radical to the 2-position, followed by cyclisation. Clearly this is not a favourable process for the initial radical. Finally the formation of 8-methylpyrrolo[1,2-a]quinoline 19 requires rearrangement of the vinyl group from the 3-position to the 2-position of the pyrrole, followed by cyclisation. Such 1,5-shifts are well-known in the thermal chemistry of pyrroles, and although the rearrangement is not normally quantitative at temperatures as low as 750 °C in our apparatus, they may well account for the formation of such a minor product (5%).

References

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3. B. R. D’Arcy, K. G. Lewis and C. E. Mulquiney, *Aust. J. Chem.*, 1985, **38**, 953-965.
4. G. R. Martinez, P. R. Grieco and G. V. Srinivasan, *J. Org. Chem.*, 1981, **46**, 3760-3761.
5. K. Ogawa, Eur. Pat. Appl., EP 575923, 1993.
6. J. M. Patterson, *Synthesis* 1976, 281-304
DFT calculations of energy surfaces

1. The iminyl 1 (X = N) – pyrrol-1-yl 3 (X = N) energy surface
mi27-02

Energy = -534.049795 Ha

Cartesian Coordinates

\[
\begin{array}{ccc}
\text{C} & -3.041371 & -0.098898 \\
\text{C} & -1.798626 & 0.516948 \\
\text{N} & -0.824730 & -0.456447 \\
\text{C} & -1.454297 & -1.657409 \\
\text{C} & -2.823808 & -1.468448 \\
\text{C} & -1.555645 & 1.912875 \\
\text{C} & 1.237008 & 0.605989 \\
\text{C} & 2.628621 & 0.713203 \\
\text{C} & 3.384003 & -0.091995 \\
\text{C} & 0.597369 & -0.304639 \\
\text{C} & 1.348210 & -1.109017 \\
\text{C} & 2.741198 & -1.004674 \\
\text{N} & -0.467255 & 2.542078 \\
\text{H} & -3.997836 & 0.405034 \\
\text{H} & -0.865528 & -2.544983 \\
\text{H} & -3.576884 & -2.234936 \\
\text{H} & -2.494089 & 2.482683 \\
\text{H} & 0.645838 & 1.222527 \\
\text{H} & 3.124433 & 1.427805 \\
\text{H} & 4.472598 & -0.006488 \\
\text{H} & 0.835689 & -1.802085 \\
\text{H} & 3.323703 & -1.632576 \\
\end{array}
\]
Energy = -534.0185255 Ha

Cartesian Coordinates

| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | -3.123748 | 0.108241 | 0.000721 |
| C       | -1.852220 | 0.665420 | -0.001048 |
| N       | -0.926150 | -0.354882 | -0.001769 |
| C       | -1.573990 | -1.561884 | -0.000418 |
| C       | -2.940701 | -1.303851 | 0.000855 |
| C       | -1.143705 | 1.930683 | -0.000201 |
| C       | 1.201830  | -0.181473 | 1.234362 |
| C       | 2.578529  | -0.285502 | 1.220211 |
| C       | 3.285336  | -0.313530 | 0.001086 |
| C       | 0.472952  | 0.016423  | -0.000762 |
| C       | 1.203402  | -0.181790 | -1.234886 |
| C       | 2.580069  | -0.285847 | -1.218969 |
| N       | 0.135402  | 1.911171  | 0.000128 |
| H       | -4.067437 | 0.647879  | 0.001437 |
| H       | -1.024939 | -2.499258 | -0.000733 |
| H       | -3.723364 | -2.059262 | 0.001781 |
| H       | -1.677148 | 2.894766  | 0.000744 |
| H       | 0.638916  | -0.183402 | 2.169073 |
| H       | 3.122484  | -0.374880 | 2.163434 |
| H       | 4.373316  | -0.402248 | 0.001767 |
| H       | 0.641586  | -0.183850 | -2.170263 |
| H       | 3.125298  | -0.375119 | -2.161466 |

Calculated Negative Frequency = -586.6398 cm⁻¹
Energy = -534.0339942 Ha

Cartesian Coordinates

C  -3.093562  -0.160440  0.000084
C  -1.912580   0.574629  -0.000265
N   -0.853460  -0.306091  -0.000984
C   -1.310808  -1.591039  -0.001181
C   -2.705023  -1.529678  -0.000581
C   -1.298663   1.886410  0.001112
C    1.219619   0.152598  1.258521
C    2.497840  -0.330833  1.228591
C    3.165334  -0.581955  0.000006
C    0.439742   0.442051  0.000207
C    1.220493   0.155141 -1.258327
C    2.498662  -0.328383 -1.228530
N    -0.003824   1.868341  0.001276
H    -4.106755   0.233508  -0.000021
H    -0.637061  -2.443267  -0.001801
H    -3.370015  -2.391059  -0.000258
H    -1.843777   2.834995  0.001857
H     0.703503   0.356114   2.198617
H     3.018221  -0.527247   2.169504
H     4.185790  -0.968163  -0.000013
H     0.705061   0.361162  -2.198247
H     3.019689  -0.522807  -2.169500
mi33

Energy = -534.0172811 Ha

Cartesian Coordinates

\[
\begin{array}{ccc}
C & 3.095544 & -0.149778 \\
C & 1.851619 & 0.504613 \\
N & 0.859734 & -0.433898 \\
C & 1.408297 & -1.664957 \\
C & 2.810847 & -1.529321 \\
C & 1.322842 & 1.833420 \\
C & -1.434649 & 0.463876 \\
C & -2.522047 & -0.379184 \\
C & -2.998485 & -0.892030 \\
C & -0.709648 & 0.790751 \\
C & -1.286253 & 0.317151 \\
C & -2.379235 & -0.521580 \\
N & 0.032166 & 1.973188 \\
H & 4.074071 & 0.321186 \\
H & 0.805170 & -2.567335 \\
H & 3.528902 & -2.348418 \\
H & 1.955760 & 2.724855 \\
H & -1.067369 & 0.897235 \\
H & -3.035463 & -0.638997 \\
H & -3.867408 & -1.552929 \\
H & -0.808468 & 0.641119 \\
H & -2.781488 & -0.889516
\end{array}
\]

Calculated Negative Frequency = -289.7431 cm\(^{-1}\)
Energy = -534.0465458 Ha

Cartesian Coordinates

|   |        |        |        |
|---|--------|--------|--------|
| C | 3.390535 | -0.766795 | -0.000228 |
| C | 1.962627 | -0.438826 | -0.000178 |
| N | 1.788536 | 0.934910  | 0.000568  |
| C | 3.008870 | 1.444683  | 0.000863  |
| C | 4.054308 | 0.424395  | 0.000422  |
| C | -1.332129| -0.607345 | -0.000205 |
| C | -2.640224| -1.168709 | 0.000715  |
| C | -3.772804| -0.365143 | 0.000897  |
| C | -1.209316| 0.808512  | -0.001019 |
| C | -2.352770| 1.602481  | -0.000890 |
| C | -3.632578| 1.029703  | 0.000071  |
| C | 0.979562 | -1.468742 | -0.000671 |
| N | -0.336112| -1.562987 | -0.000395 |
| H | 3.808012 | -1.772154 | -0.000705 |
| H | 3.163460 | 2.526628  | 0.001413  |
| H | 5.128506 | 0.600659  | 0.000589  |
| H | -2.711683| -2.257575 | 0.001259  |
| H | -4.766454| -0.818317 | 0.001639  |
| H | -0.214245| 1.254468  | -0.001552 |
| H | -2.247310| 2.690061  | -0.001515 |
| H | -4.518371| 1.669439  | 0.000168  |
| H | 1.454629 | -2.461952 | -0.001167 |
Energy = -534.0274203 Ha

Cartesian Coordinates

| Atom | X     | Y       | Z       |
|------|-------|---------|---------|
| C    | -3.092837 | 0.325229 | -0.171449 |
| C    | -1.712262 | 0.601515 | -0.019988 |
| N    | -1.008065 | -0.584377 | -0.142644 |
| C    | -1.887028 | -1.585495 | -0.273030 |
| C    | -3.205557 | -1.061192 | -0.326070 |
| C    | 1.101996  | 0.930347  | 0.199588  |
| C    | 2.313239  | 1.027315  | -0.514940 |
| C    | 3.136343  | -0.079205 | -0.669526 |
| C    | 0.745762  | -0.338404 | 0.817131  |
| C    | 1.644969  | -1.442307 | 0.683706  |
| C    | 2.794237  | -1.318513 | -0.068946 |
| C    | -1.037050 | 1.827416  | 0.243363  |
| N    | 0.262764  | 2.012776  | 0.248377  |
| H    | -3.896317 | 1.059870  | -0.168179 |
| H    | -1.561268 | -2.620477 | -0.374192 |
| H    | -4.113003 | -1.634425 | -0.508815 |
| H    | 2.556794  | 1.988939  | -0.969878 |
| H    | 4.056055  | 0.002866  | -1.252230 |
| H    | 0.131932  | -0.292222 | 1.718884  |
| H    | 1.416584  | -2.376066 | 1.201399  |
| H    | 3.472876  | -2.168878 | -0.169235 |
| H    | -1.657430 | 2.721369  | 0.383089  |

Calculated Negative Frequency = -318.7850 cm⁻¹
Energy = -534.0568049 Ha

Cartesian Coordinates

| Element | x     | y     | z     |
|---------|-------|-------|-------|
| C       | -3.012740 | 0.308616 | -0.234305 |
| C       | -1.683373 | 0.685839 | -0.006164 |
| N       | -0.929725 | -0.471882 | 0.103537 |
| C       | -1.750814 | -1.557455 | -0.017505 |
| C       | -3.048602 | -1.103123 | -0.245363 |
| C       | -1.011227 | 1.945320 | 0.070189 |
| C       | 1.058935 | 0.947424 | 0.124832 |
| C       | 2.423941 | 1.021641 | -0.182699 |
| C       | 3.209399 | -0.119395 | -0.308536 |
| C       | 0.468052 | -0.389608 | 0.566442 |
| C       | 1.316028 | -1.574749 | 0.191784 |
| C       | 2.618470 | -1.419160 | -0.164084 |
| N       | 0.299376 | 2.076976 | 0.076565 |
| H       | -3.842588 | 0.991767 | -0.399937 |
| H       | -1.372167 | -2.571918 | 0.057813 |
| H       | -3.915890 | -1.736456 | -0.415491 |
| H       | 2.830025 | 2.015172 | -0.383795 |
| H       | 4.262748 | -0.033605 | -0.579945 |
| H       | 0.888195 | -2.571990 | 0.311315 |
| H       | 3.230849 | -2.303241 | -0.359238 |
| H       | 0.414560 | -0.358350 | 1.683686 |
| H       | -1.611708 | 2.860859 | 0.057317 |
mi32-07

Energy = -534.0267681 Ha

Cartesian Coordinates

\[
\begin{align*}
C & : 3.010825, 0.314594, -0.151556 \\
C & : 1.665107, 0.662901, -0.136472 \\
N & : 0.937338, -0.476961, 0.189577 \\
C & : 1.804066, -1.529139, 0.365073 \\
C & : 3.096322, -1.065081, 0.175089 \\
C & : 0.968373, 1.889474, -0.498931 \\
C & : -0.476313, -0.463210, 0.165578 \\
C & : -1.219186, -1.455559, -0.464243 \\
C & : -2.612362, -1.329120, -0.549678 \\
C & : -1.086635, 0.728305, 0.684168 \\
C & : -2.517572, 0.810063, 0.594333 \\
C & : -3.249829, -0.184564, -0.026951 \\
N & : -0.264156, 2.177273, -0.334730 \\
H & : 3.834159, 0.988376, -0.377957 \\
H & : 1.433188, -2.512206, 0.641286 \\
H & : 4.001527, -1.659733, 0.269723 \\
H & : 1.594658, 2.657410, -0.993015 \\
H & : -0.710705, -2.313844, -0.907738 \\
H & : -3.198156, -2.109394, -1.038696 \\
H & : -0.611415, 1.189758, 1.554919 \\
H & : -3.015888, 1.680201, 1.025339 \\
H & : -4.336421, -0.094730, -0.096253
\end{align*}
\]

Calculated Negative Frequency = -552.9239 cm\(^{-1}\)
mi28

Energy = -534.0494495 Ha

Cartesian Coordinates

| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| C    | 3.020963 | 0.362746 | -0.142791|
| C    | 1.672684 | 0.691471 | -0.086292|
| N    | 0.954726 | -0.486981| 0.121935 |
| C    | 1.837200 | -1.542163| 0.186362 |
| C    | 3.121116 | -1.043190| 0.038725 |
| C    | 0.931069 | 1.918256 | -0.283726|
| C    | -0.445266| -0.469230| 0.111625 |
| C    | -1.035956| 0.880460 | 0.458853 |
| C    | -2.506874| 0.945942 | 0.158304 |
| C    | -1.226247| -1.570765| -0.160910|
| C    | -2.630057| -1.450749| -0.234761|
| C    | -3.243292| -0.170297| -0.115863|
| N    | -0.330831| 2.062405 | -0.085748|
| H    | 3.836868 | 1.065713 | -0.293471|
| H    | 1.489274 | -2.555673| 0.359619 |
| H    | 4.033291 | -1.634051| 0.069674 |
| H    | 1.494710 | 2.791567 | -0.640190|
| H    | -0.922010| 0.997640 | 1.569331 |
| H    | -2.958869| 1.938150 | 0.211346 |
| H    | -0.757214| -2.535102| -0.367519|
| H    | -3.235091| -2.330023| -0.459799|
| H    | -4.320263| -0.081062| -0.279463|
2. The vinyl 1 (X = CH) – pyrrol-1-yl 3 (X = CH) energy surface
mi37

Energy = -557.3385771 Ha

Cartesian Coordinates

|   |   |           |           |           |
|---|---|-----------|-----------|-----------|
| C |  3.971925 |  0.453164 |  0.000349 |
| C |  2.513530 |  0.363405 | -0.000010 |
| N |  2.119050 | -0.967791 |  0.000268 |
| C |  3.240614 | -1.668171 |  0.000006 |
| C |  4.434319 | -0.832510 |  0.000170 |
| C | -0.874761 |  0.895467 | -0.000093 |
| C | -2.127978 |  1.565715 | -0.000115 |
| C | -3.326192 |  0.866772 | -0.000122 |
| C | -0.893752 | -0.520237 | -0.000082 |
| C | -2.104251 | -1.208481 | -0.000099 |
| C | -3.340306 | -0.541193 | -0.000113 |
| C |  1.684203 |  1.503833 | -0.000062 |
| C |  0.308740 |  1.728285 | -0.000088 |
| C | -4.644952 | -1.295808 | -0.000064 |
| H |  4.548418 |  1.377060 |  0.000541 |
| H |  3.218393 | -2.760870 |  0.000027 |
| H |  5.466363 | -1.179431 |  0.000227 |
| H | -2.143885 |  2.659030 | -0.000129 |
| H | -4.271764 |  1.416031 | -0.000144 |
| H |  0.056050 | -1.057638 | -0.000108 |
| H | -2.090528 | -2.301890 | -0.000115 |
| H |  2.264816 |  2.432748 | -0.000029 |
| H |  0.059853 |  2.795568 | -0.000103 |
| H | -4.484037 | -2.383592 | -0.000701 |
| H | -5.252256 | -1.041471 | -0.885503 |
| H | -5.251600 | -1.042445 |  0.886112 |
Energy = -557.2825262 Ha

Cartesian Coordinates

|    | X   | Y   | Z   |
|----|-----|-----|-----|
| C  | 3.355660 | -0.691058 | 0.167686 |
| C  | 2.358208 | 0.269286  | -0.010235 |
| N  | 1.211791 | -0.355979 | -0.485523 |
| C  | 1.412671 | -1.691288 | -0.484250 |
| C  | 2.750135 | -1.941006 | -0.123497 |
| C  | 2.148341 | 1.665632  | 0.261209  |
| C  | -1.107408| 1.044235  | -1.109915 |
| C  | -2.323955| 0.403611  | -1.062679 |
| C  | -2.755075| -0.296052 | 0.095921  |
| C  | -0.170018| 0.964277  | -0.004819 |
| C  | -0.674159| 0.331494  | 1.198996  |
| C  | -1.906681| -0.294323 | 1.223361  |
| C  | 0.851069 | 2.045510  | 0.173105  |
| C  | -4.083030| -1.002329 | 0.110907  |
| H  | 4.376083 | -0.515469 | 0.502615  |
| H  | -0.660142| -2.387545 | -0.850423 |
| H  | 3.244734 | -2.911485 | -0.161698 |
| H  | 2.968534 | 2.354963  | 0.468754  |
| H  | -0.804076| 1.596708  | -2.001281 |
| H  | -2.990244| 0.452555  | -1.928843 |
| H  | -0.035682| 0.342043  | 2.083756  |
| H  | -2.239695| -0.785482 | 2.141583  |
| H  | 0.511490 | 3.082106  | 0.213335  |
| H  | -4.880886| -0.368658 | -0.311123 |
| H  | -4.377085| -1.294678 | 1.129677  |
| H  | -4.050402| -1.921136 | -0.502419 |

Calculated Negative Frequency = -448.8027 cm\(^{-1}\)
Energy = -557.306668 Ha

Cartesian Coordinates

| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| C       | 3.483010 | -0.416578 | -0.000064 |
| C       | 2.395625 | 0.445722  | 0.000009  |
| N       | 1.242886 | -0.316255 | 0.000128  |
| C       | 1.559039 | -1.649554 | 0.000144  |
| C       | 2.946163 | -1.740386 | 0.000033  |
| C       | 1.988872 | 1.839889  | -0.000104 |
| C       | -0.806854 | 0.274047  | -1.252264 |
| C       | -2.137314 | -0.036665 | -1.220485 |
| C       | -2.858721 | -0.193746 | 0.000007  |
| C       | 0.004730  | 0.505734  | 0.000020  |
| C       | -0.806928 | 0.274282  | 1.252296  |
| C       | -2.137401 | -0.036437 | 1.220495  |
| C       | 0.639858  | 1.912277  | -0.000100 |
| C       | -4.311177 | -0.577248 | -0.000058 |
| H       | 4.533608  | -0.136768 | -0.000160 |
| H       | 0.794025  | -2.420687 | 0.000254  |
| H       | 3.514229  | -2.668352 | 0.000037  |
| H       | 2.676267  | 2.685474  | -0.000181 |
| H       | -0.273605 | 0.382753  | -2.199038 |
| H       | -2.670036 | -0.179117 | -2.165726 |
| H       | -0.273741 | 0.383166  | 2.199085  |
| H       | -2.670179 | -0.178709 | 2.165731  |
| H       | 0.018371  | 2.805689  | -0.000154 |
| H       | -4.438479 | -1.677074 | -0.001102 |
| H       | -4.832213 | -0.194465 | -0.891901 |
| H       | -4.831863 | -0.196137 | 0.892689  |
Energy = -557.2704077 Ha

Cartesian Coordinates

C  3.540535  -0.013799  -0.000046
C  2.302708   0.611522  -0.000001
N  1.326172  -0.369652  -0.000002
C  1.926297  -1.610655  -0.000046
C  3.297719  -1.419267  -0.000076
C  1.776755   1.964779   0.000064
C -0.809122  -0.173533  -1.221496
C -2.195501  -0.200168  -1.208144
C -2.922829  -0.190729   0.000035
C -0.079694  -0.051055   0.000035
C -0.809100  -0.173739  1.221527
C -2.195513  -0.200347  1.208175
C  0.451746   2.074149   0.000107
C -4.430211  -0.185936  -0.000065
H  4.506687   0.485178  -0.000053
H  1.329790  -2.518523  -0.000057
H  4.045057  -2.209515  -0.000113
H  2.468663   2.817303   0.000080
H -0.253467  -0.208585  -2.159892
H -2.736890  -0.255451  -2.156607
H -0.253452  -0.208955  2.159920
H -2.736901  -0.255761  2.156627
H -0.275884   2.883495   0.000161
H -4.825606   0.846151  -0.003296
H -4.837018  -0.684849   0.893306
H -4.836915  -0.690257  -0.890475

Calculated Negative Frequency = -449.1627 cm\(^{-1}\)
Energy = -557.2819893 Ha

Cartesian Coordinates

|   |   |   |   |
|---|---|---|---|
| C | -3.472610 | -0.042161 | 0.081226 |
| C | -2.221364 | 0.554226 | -0.048936 |
| N | -1.272326 | -0.461539 | 0.039960 |
| C | -1.922221 | -1.667958 | 0.218778 |
| C | -3.283784 | -1.438908 | 0.248350 |
| C | -1.956456 | 1.967316 | -0.311244 |
| C | 0.804900 | 0.293012 | 1.108942 |
| C | 2.197355 | 0.393744 | 1.109104 |
| C | 2.967157 | -0.131833 | 0.059530 |
| C | 0.151016 | -0.330426 | 0.040382 |
| C | 0.901810 | -0.863914 | -1.013534 |
| C | 2.294243 | -0.767650 | -0.996064 |
| C | -0.832841 | 2.604301 | -0.607465 |
| C | 4.471632 | -0.003972 | 0.052149 |
| H | -4.419250 | 0.491982 | 0.033834 |
| H | -1.346724 | -2.581427 | 0.339862 |
| H | -4.053041 | -2.196182 | 0.378533 |
| H | -2.876916 | 2.569267 | -0.267289 |
| H | 0.217403 | 0.695933 | 1.935322 |
| H | 2.696712 | 0.882728 | 1.949543 |
| H | 0.386576 | -1.348098 | -1.845151 |
| H | 2.869046 | -1.191215 | -1.823992 |
| H | 4.953310 | -0.931937 | -0.294476 |
| H | 4.862272 | 0.229935 | 1.053678 |
| H | 4.797782 | 0.803333 | -0.626737 |
| H | 0.226087 | 2.411788 | -0.760151 |
mi42

Energy = -557.2758494 Ha

Cartesian Coordinates

| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | 3.456492| 0.183482| -0.136936|
| C       | 2.140397| 0.628418| -0.144210|
| N       | 1.333663| -0.461343| 0.181544|
| C       | 2.130669| -1.571944| 0.377365|
| C       | 3.449002| -1.199271| 0.198914|
| C       | 1.582895| 1.923136| -0.506648|
| C       | -0.082666| -0.419296| 0.159195|
| C       | -0.827951| -1.347663| -0.564683|
| C       | -2.221023| -1.232934| -0.626383|
| C       | -0.728421| 0.670226| 0.802180|
| C       | -2.142895| 0.745989| 0.744198|
| C       | -2.896314| -0.176658| 0.019110|
| C       | 0.308818| 2.280455| -0.360538|
| C       | -4.399994| -0.069353| -0.067155|
| H       | 4.325207| 0.800585| -0.356056|
| H       | 1.687764| -2.522529| 0.660719|
| H       | 4.312132| -1.851060| 0.309843|
| H       | 2.305950| 2.625815| -0.949606|
| H       | -0.315588| -2.150724| -1.097819|
| H       | -2.792645| -1.970915| -1.194771|
| H       | -0.200951| 1.196712| 1.597951|
| H       | -2.648462| 1.546346| 1.290278|
| H       | -4.787209| 0.722888| 0.590339|
| H       | -4.887731| -1.016387| 0.216964|
| H       | -4.722375| 0.162787| -1.096803|
| H       | -0.225786| 3.198368| -0.608299|

Calculated Negative Frequency = -407.7119 cm⁻¹
mi43

Energy = -557.3249804 Ha

Cartesian Coordinates

|   |   |   |   |
|---|---|---|---|
| C | 3.456488 | 0.288210 | -0.211272 |
| C | 2.129001 | 0.678301 | -0.123412 |
| N | 1.366191 | -0.468599 | 0.126386 |
| C | 2.211766 | -1.563014 | 0.184318 |
| C | 3.505137 | -1.122055 | -0.010868 |
| C | 1.455872 | 1.946690 | -0.291624 |
| C | -0.034777 | -0.438422 | 0.151138 |
| C | -0.645275 | 0.894448 | 0.525738 |
| C | -2.123543 | 0.947853 | 0.241160 |
| C | -0.821451 | -1.539663 | -0.109481 |
| C | -2.225361 | -1.433124 | -0.156583 |
| C | -2.873801 | -0.161747 | -0.029655 |
| C | 0.142532 | 2.070641 | -0.025862 |
| C | -4.368312 | -0.079399 | -0.230180 |
| H | 4.296255 | 0.954526 | -0.394005 |
| H | 1.827300 | -2.556007 | 0.393165 |
| H | 4.393809 | -1.748499 | 0.004916 |
| H | 2.049652 | 2.793345 | -0.642791 |
| H | -0.532562 | 0.975084 | 1.642236 |
| H | -2.602265 | 1.927698 | 0.327194 |
| H | -0.353807 | -2.501055 | -0.330672 |
| H | -2.821543 | -2.322091 | -0.371939 |
| H | -4.735464 | 0.952034 | -0.125527 |
| H | -4.900223 | -0.705837 | 0.506283 |
| H | -4.656857 | -0.445515 | -1.230114 |
| H | -0.377288 | 3.024194 | -0.143952 |
mi44

Energy = -557.303685 Ha

Cartesian Coordinates

| Atoms | X    | Y    | Z    |
|-------|------|------|------|
| C     | -3.498161 | -0.232776 | -0.156683 |
| C     | -2.219679  | 0.369463  | -0.028958 |
| N     | -1.252793  | -0.626373 | -0.127706 |
| C     | -1.874679  | -1.804745 | -0.229914 |
| C     | -3.283345  | -1.608371 | -0.274915 |
| C     | 0.573833   | 1.312919  | 0.198113  |
| C     | 1.811709   | 1.653685  | -0.392742 |
| C     | 2.834278   | 0.729022  | -0.508478 |
| C     | 0.420114   | -0.020700 | 0.758976  |
| C     | 1.511745   | -0.941574 | 0.644003  |
| C     | 2.685253   | -0.596070 | 0.002694  |
| C     | -1.859159  | 1.735353  | 0.138646  |
| C     | -0.553692  | 2.190860  | 0.163780  |
| C     | 3.830401   | -1.568781 | -0.121677 |
| H     | -4.451790  | 0.292549  | -0.160498 |
| H     | -1.316231  | -2.736185 | -0.324600 |
| H     | -4.030850  | -2.383514 | -0.436435 |
| H     | 1.935200   | 2.659100  | -0.804298 |
| H     | 3.769375   | 1.008897  | -0.999615 |
| H     | -0.189524  | -0.092522 | 1.662677  |
| H     | 1.415082   | -1.925899 | 1.108694  |
| H     | -2.674938  | 2.461277  | 0.138920  |
| H     | 4.750153   | -1.163310 | 0.332883  |
| H     | 4.060246   | -1.767488 | -1.182724 |
| H     | 3.603562   | -2.529958 | 0.361917  |
| H     | -0.372437  | 3.262865  | 0.039937  |

Calculated Negative Frequency = -384.7188 cm⁻¹
mi45

Energy = -557.3344448 Ha

Cartesian Coordinates

C  -3.362922  -0.350878  -0.235863
C  -2.187768   0.388804  -0.055270
N  -1.144286  -0.515476   0.110554
C  -1.646981  -1.790231   0.068966
C  -3.016848  -1.719138  -0.159878
C  -1.911849  1.788598  -0.074258
C   0.477450   1.350033   0.120914
C   1.819982   1.729655  -0.056894
C   2.847318   0.801608  -0.096197
C   0.193635  -0.080748   0.557186
C   1.299731  -1.042138   0.206538
C   2.568013  -0.616295  -0.035693
C  -0.608853   2.243798  -0.027709
C   3.700975  -1.583805  -0.271476
H  -4.346612   0.072576  -0.425462
H  -1.010530  -2.659071   0.200054
H  -3.681100  -2.572361  -0.274728
H   2.038289   2.787650  -0.228959
H   3.875253   1.131818  -0.261607
H   1.087084  -2.111163   0.262866
H   0.135762  -0.049164   1.674731
H  -2.747176   2.478853  -0.199796
H   4.496827  -1.447290   0.481014
H   4.164319  -1.417628  -1.258987
H   3.362414  -2.629024  -0.223144
H  -0.395823   3.307557  -0.162051
References

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