Supporting Information for:

Unusual para-substituent effects on the intramolecular hydrogen-bond in hydrazone-based switches

Xin Su\textsuperscript{a}, Märt Lõkov\textsuperscript{b}, Agnes Kütt\textsuperscript{b}, Ivo Leito\textsuperscript{b} and Ivan Aprahamian\textsuperscript{a} \\
\textsuperscript{a}Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755, USA. \\
\textsuperscript{b}Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia.

E-mail: ivan.aprahamian@dartmouth.edu; ivo.leito@ut.ee \\
Website: www.dartmouth.edu/~aprahamian/
1 General

All reagents and starting materials were purchased from commercial sources and used as supplied unless otherwise indicated. All experiments were conducted in air unless otherwise noted. Column chromatography was performed on silica gel (SiliCycle®, 60 Å, 230-400 mesh). Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and used as received. NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer, with working frequencies of 299.97 MHz for $^1$H nuclei and 75.44 MHz for $^{13}$C nuclei, respectively. Chemical shifts are quoted in ppm relative to tetramethylsilane (TMS), using the residual solvent peak as the reference standard. Mass spectra were obtained either on a Shimadzu GCMS-QP2010S gas chromatograph/ EI mass spectrometer or on a Waters Quattro II ESI mass spectrometer. Melting points were measured on an Electrothermal Thermo Scientific IA9100X1 digital melting point instrument. The $pK_a$ measurements were conducted using a previously reported methodology.$^{S1,S2}$

2 Synthesis

Compound $p$-H was synthesized by following a reported procedure.$^{S3}$ All other hydrazone derivatives were synthesized in a similar manner starting from the corresponding $p$-substituted anilines and ethyl-2-pyridyl acetate.

Scheme S1: The synthesis and structures of the hydrazone derivatives with different para-substituents on the phenyl ring.

$p$-NMe$_2$: obtained as a red crystalline powder, yield 79%, m.p. 99.2 – 99.4 °C; $^1$H NMR (300 MHz, CD$_3$CN) $\delta$ 14.78 (s, N–H), 8.68 (ddd, $J = 5.0, 1.9, 1.0$ Hz, H1), 8.19 (dt, $J = 8.4, 1.0$ Hz, H4), 7.87 (ddd, $J = 8.4, 7.5, 1.9$ Hz, H3), 7.47 – 7.21 (m, H2 and H5), 6.88 – 6.70 (d, $J = 9.0$ Hz, H6), 4.30 (qd, $J = 7.1, 1.8$ Hz, –CH$_2$–), 2.89 (s, –N(CH$_3$)$_2$), 1.37 (t, $J = 7.1$ Hz, –CH$_3$)
ppm; $^{13}$C NMR (75 MHz, CD$_3$CN) δ 166.47, 153.88, 148.54, 147.55, 137.71, 134.92, 124.51, 124.36, 123.83, 122.92, 116.70, 116.37, 114.60, 61.27, 41.14, 14.64 ppm. MS (ESI): m/z found [M–H$^+$] for C$_{17}$H$_{21}$N$_4$O$_3^+$ 313.2 (calcd. 313.2).

$p$-OH: obtained as a yellow powder, yield 82%, m.p. 178.9 – 179.3 °C; $^1$H NMR (300 MHz, CD$_3$CN) δ 14.64 (s, N–H), 8.70 (d, J = 5.0 Hz, H1), 8.16 (d, J = 8.4 Hz, H4), 7.97 – 7.83 (m, H3), 7.34 (dd, J = 6.5, 5.1 Hz, H2), 7.24 (d, J = 8.9 Hz, H5), 6.83 (d, J = 8.9 Hz, H6), 6.74 (s, –OH), 4.31 (q, J = 7.1 Hz, –CH$_2$–), 1.37 (t, J = 7.1 Hz, –CH$_3$) ppm; $^{13}$C NMR (75 MHz, CD$_3$CN) δ 166.38, 153.84, 153.67, 147.71, 137.84, 137.47, 137.18, 125.29, 124.71, 123.23, 116.88, 116.83, 116.51, 61.41, 14.62 ppm. MS (ESI): m/z found [M–H$^+$] for C$_{15}$H$_{16}$N$_3$O$_2$ 286.1 (calcd. 286.1).

$p$-OnHex: obtained as bright yellow flakes, yield 89%, m.p. 74.0 – 74.4 °C; $^1$H NMR (300 MHz, CD$_3$CN) δ 14.67 (s, N–H), 8.75 – 8.66 (m, H1), 8.16 (d, J = 8.4 Hz, H4), 7.87 (ddd, J = 24.0, 12.6, 8.7 Hz, H3), 7.36 – 7.27 (m, H2 and H5), 6.90 (dd, J = 10.3, 5.6 Hz, H6), 4.31 (q, J = 7.1 Hz, –OCH$_2$CH$_3$), 3.94 (dd, J = 9.0, 4.1 Hz, –OCH$_2$CH$_2$CH$_2$CH$_3$ and –OCH$_2$CH$_3$), 0.91 (dd, J = 9.6, 4.3 Hz, –CH$_2$CH$_2$CH$_3$) ppm; $^{13}$C NMR (75 MHz, CD$_3$CN) δ 166.34, 153.84, 153.67, 147.71, 137.84, 137.47, 137.18, 125.29, 124.71, 123.23, 116.88, 116.83, 116.51, 61.41, 14.62 ppm. MS (ESI): m/z found M$^+$ for C$_{21}$H$_{27}$N$_3$O$_3$ 369 (calcd. 369).

$p$-OMe: obtained as a dark yellow powder, yield 69%, m.p. 71.9 – 72.3 °C; $^1$H NMR (300 MHz, CD$_3$CN) δ 14.66 (s, N–H), 8.70 (ddd, J = 5.0, 1.8, 0.9 Hz, H1), 8.15 (dt, J = 8.3, 0.9 Hz, H4), 7.88 (ddd, J = 8.4, 7.6, 1.9 Hz, H3), 7.39 – 7.27 (m, H2 and H5), 6.94 (d, J = Hz, H6), 4.31 (q, J = 7.1 Hz, –CH$_2$–), 3.77 (s, –OCH$_3$), 1.37 (t, J = 7.1 Hz, –CH$_2$CH$_3$) ppm; $^{13}$C NMR (75 MHz, CD$_3$CN) δ 166.35, 156.16, 153.55, 147.69, 137.93, 137.83, 125.53, 124.71, 123.26, 116.64, 116.36, 116.21, 69.06, 61.43, 32.23, 29.92, 26.34, 23.24, 14.59, 14.25 ppm. MS (EI): m/z found M$^+$ for C$_{21}$H$_{27}$N$_3$O$_3$ 369 (calcd. 369).

$p$-F: obtained as a bright yellow powder, yield 75%, m.p. 61.7 – 62.0 °C; $^1$H NMR (300 MHz, CD$_3$CN) δ 14.60 (s, N–H), 8.71 (ddd, J = 5.0, 1.8, 1.0 Hz, H1), 8.12 (dt, J = 8.3, 1.0 Hz, H4), 7.90 (ddd, J = 8.4, 7.6, 1.9 Hz, H3), 7.46 – 7.33 (m, H2 and H5), 7.17 – 7.02 (m, H6), 4.33
(qd, J = 7.1, 1.9 Hz, –CH₂–), 1.38 (t, J = 7.2 Hz, –CH₃) ppm; ¹³C NMR (75 MHz, CD₃CN) δ 166.17, 161.11, 157.95, 153.20, 147.89, 140.95, 138.01, 129.91, 124.98, 123.69, 116.94, 116.75, 116.65, 61.65, 14.55 ppm. MS (EI): m/z found M⁺ for C₁₅H₁₄FN₃O₂⁺ 287 (calcd. 287).

**p-Cl**: obtained as a bright yellow powder, yield 81%, m.p. 85.9 – 86.3 °C; ¹H NMR (300 MHz, CD₃CN) δ 14.58 (s, N–H), 8.72 (ddd, J = 5.0, 1.9, 1.0 Hz, H1), 8.10 (dt, J = 8.3, 1.0 Hz, H4), 7.98 – 7.84 (m, H3), 7.49 – 7.17 (m, H2, H5 and H6), 4.32 (qd, J = 7.2, 4.2 Hz, –CH₂–), 1.36 (t, J = 7.2 Hz, –CH₃) ppm; ¹³C NMR (75 MHz, CD₃CN) δ 166.07, 152.99, 147.98, 143.35, 138.75, 138.08, 130.14, 127.57, 125.14, 124.19, 117.66, 116.73, 61.77, 14.52 ppm. MS (EI): m/z found M⁺ for C₁₅H₁₄ClN₃O₂⁺ 303 (calcd. 303) and C₁₅H₁₄ClN₃O₂⁺ 305 (calcd. 305).

**p-Br**: obtained as a bright yellow powder, yield 83%, m.p. 91.5 – 92.0 °C; ¹H NMR (300 MHz, CD₃CN) δ 14.57 (s, 1H), 8.78 – 8.66 (m, H1), 8.10 (dt, J = 8.3, 1.0 Hz, H4), 7.98 – 7.84 (m, H3), 7.54 – 7.45 (m, H6), 7.39 (ddd, J = 7.5, 5.0, 1.1 Hz, H2), 7.33 – 7.25 (m, H5), 4.33 (qd, J = 7.1, 2.8 Hz, –CH₂–), 1.37 (t, J = 7.2 Hz, –CH₃) ppm; ¹³C NMR (75 MHz, CD₃CN) δ 166.07, 153.02, 149.61, 148.03, 143.83, 138.12, 133.11, 128.05, 125.20, 123.95, 117.15, 116.83, 115.04, 61.80, 14.56 ppm. MS (EI): m/z found M⁺ for C₁₅H₁₄BrN₃O₂⁺ 347 (calcd. 347) and C₁₅H₁₄BrN₃O₂⁺ 349 (calcd. 350).

**p-MC**: obtained as a bright yellow powder, yield 80%, m.p. 92.7 – 93.1 °C; ¹H NMR (300 MHz, CD₃CN) δ 14.64 (s, N–H), 8.79 – 8.70 (m, H1), 8.07 (dt, J = 8.3, 1.0 Hz, 4H), 8.02 – 7.87 (m, H3), 7.47 – 7.36 (m, H2 and H6), 4.35 (qd, J = 7.1, 1.9 Hz, –CH₂–), 3.84 (s, –OCH₃), 1.38 (t, J = 7.2 Hz, –CH₂CH₃) ppm; ¹³C NMR (75 MHz, CD₃CN) δ 167.31, 165.95, 152.69, 148.32, 148.20, 138.25, 131.98, 129.71, 125.44, 124.60, 124.29, 116.11, 114.79, 52.37, 14.53 ppm. MS (EI): m/z found M⁺ for C₁₇H₁₇N₃O₂⁺ 327 (calcd. 327).

**p-CN**: obtained as a bright yellow powder, yield 80%, m.p. 95.7 – 95.9 °C; ¹H NMR (300 MHz, CD₃CN) δ 14.65 (s, N–H), 8.84 – 8.65 (m, H1), 8.06 (d, J = 8.3 Hz, H4), 7.99 – 7.88 (m, H3), 7.65 (d, J = 7.7 Hz, H5), 7.49 – 7.28 (m, H2 and H6), 4.35 (q, J = 7.1 Hz, –CH₂–), 1.38 (t, J = 7.1 Hz, –CH₃) ppm; ¹³C NMR (75 MHz, CD₃CN) δ 165.80, 152.40, 150.76, 149.56, 148.22, 138.30, 135.13, 134.65, 129.90, 125.51, 124.48, 120.18, 115.46, 105.07, 62.09, 14.46 ppm. MS (EI): m/z found M⁺ for C₁₆H₁₄N₄O₂⁺ 294 (calcd. 294).
p-NO$_2$: obtained as a bright yellow powder, yield 77%, m.p. 124.2 – 124.5 °C; $^1$H NMR (300 MHz, CD$_3$CN) $\delta$ 14.77 (s, N–H), 8.75 (ddd, $J$= 4.9, 1.8, 1.0 Hz, H1), 8.25 – 8.13 (m, H6), 8.05 (dt, $J$= 8.2, 1.0 Hz, H4), 7.99 – 7.90 (m, H3), 7.49 – 7.38 (m, H2 and H5), 4.37 (dq, $J$= 14.2, 7.0 Hz, –CH$_2$–), 1.39 (t, $J$= 7.1 Hz, –CH$_3$) ppm; $^{13}$C NMR (75 MHz, CD$_3$CN) $\delta$ 201.96, 165.68, 152.17, 149.87, 148.28, 142.90, 138.36, 131.51, 126.55, 125.61, 124.66, 114.77, 114.42, 110.52, 62.19, 14.42 ppm. MS (EI): $m/z$ found M$^+$ for C$_{15}$H$_{14}$N$_4$O$_4^+$ 314 (calcd. 314).

3 Summary of Analyzed Data

Table S1: A summary of Hammett constants, chemical shifts (CD$_3$CN), N···N distances and p$K_a$ values.

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<th></th>
<th>$\sigma_p$</th>
<th>$\delta_{N\cdot\cdot\cdotH,Z}$/ppm</th>
<th>$\delta_{N\cdot\cdot\cdotH,E}$/ppm</th>
<th>$\delta_{H5}$/ppm</th>
<th>$d$(N···N)/Å</th>
<th>p$K_a$</th>
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<tr>
<td>p-NMe$_2$</td>
<td>-0.83</td>
<td>11.85</td>
<td>14.78</td>
<td>8.68</td>
<td>2.6349(14)</td>
<td>13.39</td>
</tr>
<tr>
<td>p-OH</td>
<td>-0.37</td>
<td>11.67</td>
<td>14.64</td>
<td>8.69</td>
<td>-</td>
<td>12.92</td>
</tr>
<tr>
<td>p-OnHex</td>
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<td>14.67</td>
<td>8.69</td>
<td>2.6312(37)</td>
<td>12.86</td>
</tr>
<tr>
<td>p-OMe</td>
<td>-0.27</td>
<td>11.66</td>
<td>14.66</td>
<td>8.70</td>
<td>-</td>
<td>12.82</td>
</tr>
<tr>
<td>p-H</td>
<td>0</td>
<td>11.48</td>
<td>14.55</td>
<td>8.72</td>
<td>2.6580(23)</td>
<td>12.26</td>
</tr>
<tr>
<td>p-F</td>
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<td>11.46</td>
<td>14.60</td>
<td>8.71</td>
<td>-</td>
<td>12.26</td>
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<tr>
<td>p-Cl</td>
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<td>14.58</td>
<td>8.72</td>
<td>2.6198(32)</td>
<td>12.08</td>
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<td>p-CN</td>
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<td>8.74</td>
<td>-</td>
<td>11.4</td>
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<tr>
<td>p-NO$_2$</td>
<td>0.78</td>
<td>11.16</td>
<td>14.77</td>
<td>8.75</td>
<td>2.6027(16)</td>
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## 4 pK\textsubscript{a} Measurements Data

Table S2: Results of the experimental pK\textsubscript{a} measurements.

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<th>Base (B)</th>
<th>Reference base (RB)</th>
<th>pK\textsubscript{a}</th>
<th>∆pK\textsubscript{a}</th>
<th>pK\textsubscript{a} (B)</th>
<th>Assigned</th>
</tr>
</thead>
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<tr>
<td><strong>p-NMe\textsubscript{2}</strong></td>
<td>2-Me-Pyridine</td>
<td>13.32</td>
<td>-0.09</td>
<td>13.41</td>
<td>13.39</td>
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<td></td>
<td>2,6-Me\textsubscript{2}-Pyridine</td>
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<td>0.76</td>
<td>13.37</td>
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<td>-0.36</td>
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<td>2-Me-Pyridine</td>
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<td>0.38</td>
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<tr>
<td><strong>p-OnHex</strong></td>
<td>Pyridine</td>
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<td>-0.28</td>
<td>12.81</td>
<td>12.86</td>
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<td>13.32</td>
<td>0.38</td>
<td>12.94</td>
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<tr>
<td><strong>p-OMe</strong></td>
<td>2-Me-Pyridine</td>
<td>13.32</td>
<td>0.47</td>
<td>12.85</td>
<td>12.82</td>
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<tr>
<td><strong>p-Cl</strong></td>
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<td><strong>p-MC</strong></td>
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<td>N,N-Me\textsubscript{2}-Aniline</td>
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<td><strong>p-NO\textsubscript{2}</strong></td>
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<td>10.50</td>
<td>0.71</td>
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\(a\) pK\textsubscript{a} values of reference bases were taken from Refs. S1 and S2.
5 Analysis Plots

Figure S1: The plot of $\delta_{N-H, Z}$ of the different derivatives (Z configuration) vs. the corresponding $\sigma_p$ values, and the linear regression fitting results.

Figure S2: The plot of $\delta_{N-H, E}$ of the different derivatives (E configuration) vs. the corresponding $\sigma_p$ values, and the linear regression fitting results.
Figure S3: The plot of δH5 of the different derivatives vs. the corresponding σp values, and the linear regression fitting results.

Figure S4: The plot of the pKₐs of the different derivatives vs. the corresponding σp values, and the linear regression fitting results.
Figure S5: The plot of $\delta_{N-H,E}$ of the different derivatives (E configuration) vs. the corresponding pK$_a$ values.

Figure S6: The plot of the predicted pK$_a$ values of the different derivatives vs. the corresponding experimental pK$_a$ values, and the linear regression fitting results.
6 Single Crystal Diffraction

Data were collected using a Bruker CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using $\omega$ and $\phi$ scans of 0.5° per frame for 30 s. The total number of images was based on results from the program COSMO$^S_4$ where redundancy was expected to be 4.0 and completeness of 100% out to 0.83 Å. Cell parameters were retrieved using APEX II software$^S_5$ and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software$^S_6$ which corrects for $L_p$. Scaling and absorption corrections were applied using SADABS$^S_7$ multi-scan technique, supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97 program and refined by least squares method on $F^2$, SHELXL-97, which are incorporated in SHELXTL-PC V 6.10.$^S_8$ All non-hydrogen atoms are refined anisotropically. All hydrogens were calculated by geometrical methods and refined as a riding model.

![Figure S7](image_url)  
Figure S7: Ball-stick drawings of the crystal structures of $p$-NMe$_2$(a), $p$-OnHex(b), $p$-Cl(c), $p$-Br(d) and $p$-NO$_2$(e).
Table S3: Crystal data and parameters for $p$-NMe$_2$, $p$-OnHex, $p$-Cl, $p$-Br and $p$-NO$_2$.

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<th>$p$-OnHex</th>
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<tr>
<td>CCDC</td>
<td>885513</td>
<td>885514</td>
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<tr>
<td>Empirical formula</td>
<td>$C_{17}H_{20}N_4O_2$</td>
<td>$C_{21}H_{25}N_3O_3$</td>
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<td>369.46</td>
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<td>173(2) K</td>
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<td>P2$_1$/c</td>
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<tr>
<td>Unit cell dimensions</td>
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<td>$a = 21.5273(7)$ Å</td>
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<td></td>
<td>$\alpha = 90^\circ$</td>
<td>$\alpha = 90^\circ$</td>
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<tr>
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<td>$\beta = 96.137(3)^\circ$</td>
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<tr>
<td></td>
<td>$c = 11.1814(8)$ Å</td>
<td>$c = 6.4359(2)$ Å</td>
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<tr>
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<td>$\gamma = 90^\circ$</td>
<td>$\gamma = 90^\circ$</td>
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<tr>
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<td>1982.67(11) Å$^3$</td>
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<tr>
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<td>664</td>
<td>792</td>
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<td>$0.20 \times 0.14 \times 0.08$ mm$^3$</td>
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<tr>
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<tr>
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<td></td>
<td>$-9 \leq k \leq 9$</td>
<td>$-14 \leq k \leq 16$</td>
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<td>$-7 \leq l \leq 7$</td>
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<td>14479</td>
</tr>
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<td>3505 [R$_{int} = 0.0981$]</td>
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<tr>
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<td>99.9%</td>
<td>96.7%</td>
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<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
<td>Semi-empirical from equivalents</td>
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<td>Max. and min. transmission</td>
<td>0.9849 and 0.9685</td>
<td>0.9500 and 0.8743</td>
</tr>
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<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
<td>Full-matrix least-squares on $F^2$</td>
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<td>Data / restraints / parameters</td>
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<td>3505 / 0 / 352</td>
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<td>1.014</td>
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<td>$R_1 = 0.0594, \omega R_2 = 0.1154$</td>
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<td>0.437 and -0.238 e⋅Å$^{-3}$</td>
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<td>p-Br</td>
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<td>885516</td>
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<td>(C_{15}H_{14}BrN_3O_2)</td>
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<td>173(2) K</td>
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<td>0.71073 Å</td>
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<td>Crystal system</td>
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<td>Orthorhombic</td>
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<tr>
<td>Space group</td>
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<td>(P2_1\bar{2}1)</td>
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<td>(c = 29.425(2) \text{Å}) (\gamma = 90°)</td>
<td>(c = 20.1172(6) \text{Å}) (\gamma = 90°)</td>
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<td>4</td>
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<td>(F_{000})</td>
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<td>(0.29 \times 0.19 \times 0.10 \text{mm}^3)</td>
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<td>2.21 to 25.38°</td>
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<td>Index ranges</td>
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<td>(-10 \leq k \leq 12)</td>
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<td></td>
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<td>(-24 \leq l \leq 19)</td>
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<td>Reflections collected</td>
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<td>7614</td>
</tr>
<tr>
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<td>2590 ([R_{int} = 0.0307])</td>
<td>2644 ([R_{int} = 0.0269])</td>
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<tr>
<td>Completeness to (\theta = 25.36°)</td>
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<td>100.0%</td>
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<td>Semi-empirical from equivalents</td>
<td>Semi-empirical from equivalents</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.9781 and 0.9233</td>
<td>0.7623 and 0.4948</td>
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<td>Full-matrix least-squares on (F^2)</td>
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<td>0.000(9)</td>
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<tr>
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<td>(R_1 = 0.0310, \omega R_2 = 0.0556)</td>
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<td>0.674 and -0.302 (\text{e} \cdot \text{Å}^{-3})</td>
<td>0.200 and -0.310 (\text{e} \cdot \text{Å}^{-3})</td>
</tr>
<tr>
<td></td>
<td>( p)-NO(_2)</td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>------------------</td>
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</tr>
<tr>
<td><strong>CCDC</strong></td>
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<tr>
<td><strong>Empirical formula</strong></td>
<td>C(<em>{15})H(</em>{14})N(_4)O(_2)</td>
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<tr>
<td><strong>Formula weight</strong></td>
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<td><strong>Temperature</strong></td>
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<td><strong>Wavelength</strong></td>
<td>0.71073 Å</td>
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<td><strong>Crystal system</strong></td>
<td>Orthorhombic</td>
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<tr>
<td><strong>Space group</strong></td>
<td>Pbca</td>
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| **Unit cell dimensions** | \( a = 6.6841(5) \text{ Å} \) \(\alpha = 90^\circ\)  
\( b = 19.9101(15) \text{ Å} \) \(\beta = 90^\circ\)  
\( c = 22.7748(17) \text{ Å} \) \(\gamma = 90^\circ\) |
| **Volume**             | 3030.9(4) Å\(^3\) |
| **Z**                  | 8                |
| **Density (calcd.)**   | 1.378 Mg·m\(^{-3}\) |
| **Absorption coefficient** | 0.103 mm\(^{-1}\) |
| **\( F_{000} \)**      | 1312             |
| **Crystal size**       | \( 0.46 \times 0.10 \times 0.08 \text{ mm}^3 \) |
| **\( \theta \) range for data collection** | 1.79 to 26.46° |
| **Index ranges**       | \(-8 \leq h \leq 8\) \(-23 \leq k \leq 24\) \(-28 \leq l \leq 28\) |
| **Reflections collected** | 24984            |
| **Independent reflections** | 3134 \([R_{\text{int}} = 0.0449]\) |
| **Completeness to \( \theta = 25.36^\circ \)** | 99.9% |
| **Absorption correction** | Semi-empirical from equivalents |
| **Max. and min. transmission** | 0.9920 and 0.9542 |
| **Refinement method**  | Full-matrix least-squares on \( F^2 \) |
| **Data / restraints / parameters** | 3134 / 0 / 264 |
| **Goodness-of-fit on \( F^2 \)** | 1.011 |
| **Final \( R \) indices \([I > 2\sigma(I)]\)** | \( R_1 = 0.0360, \omega R_2 = 0.0836 \) |
| **\( R \) indices (all data)** | \( R_1 = 0.0573, \omega R_2 = 0.0954 \) |
| **Largest diff. peak and hole** | \( 0.162 \text{ and } -0.187 \text{ e·Å}^{-3} \) |
7 Computational Methods

Calculations were performed using density functional theory (DFT) with the B3LYP functional as implemented in Gaussian 09. Geometry optimizations and frequency analysis were performed using the 6-311+G(d) basis set. NBO calculations were done using the B3LYP optimized structures.

Table S4: A summary of the NBO calculated charge distributions on the N–H and the pyridyl nitrogens in \(p\)-NMe\(_2\), \(p\)-H and \(p\)-NO\(_2\).

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<th>N–H Nitrogen</th>
<th>Pyridyl Nitrogen</th>
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<td>-0.536</td>
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<td>(p)-H</td>
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<td>-0.526</td>
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<tr>
<td>(p)-NO(_2)</td>
<td>-0.345</td>
<td>-0.530</td>
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</table>

Figure S8: Ball-and-stick drawing of the B3LYP/6-311+G(d) optimized structure of \(p\)-NMe\(_2\). The NBO calculated charge distribution is shown as well.
Figure S9: Ball-and-stick drawing of the B3LYP/6-311+G(d) optimized structure of $p$-H. The NBO calculated charge distribution is shown as well.

Figure S10: Ball-and-stick drawing of the B3LYP/6-311+G(d) optimized structure of $p$-NO$_2$. The NBO calculated charge distribution is shown as well.
Table S5: Cartesian coordinates for the B3LYP/6-311+G(d) optimized structure of $p$-NMe$_2$.

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<th>Z (Å)</th>
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Table S6: Cartesian coordinates for the B3LYP/6-311+G(d) optimized structure of \( p\)-H.

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Table S7: Cartesian coordinates for the B3LYP/6-311+G(d) optimized structure of $p$-NO$_2$.

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8 NMR Spectra

Figure S11: $^1$H NMR spectrum of $p$-NM$_2$ in CD$_3$CN at 294 K in the presence of the minor Z isomer.

Figure S12: $^{13}$C NMR spectrum of $p$-NM$_2$ in CD$_3$CN at 294 K in the presence of the minor Z isomer.
Figure S13: $^1$H NMR spectrum of $p$-OH in CD$_3$CN at 294 K in the presence of the minor Z isomer.

Figure S14: $^{13}$C NMR spectrum of $p$-OH in CD$_3$CN at 294 K in the presence of the minor Z isomer.
Figure S15: $^1$H NMR spectrum of $p$-OnHex in CD$_3$CN at 294 K in the presence of the minor Z isomer.

Figure S16: $^{13}$C NMR spectrum of $p$-OnHex in CD$_3$CN at 294 K in the presence of the minor Z isomer.
Figure S17: $^1$H NMR spectrum of p-OMe in CD$_3$CN at 294 K in the presence of the minor Z isomer.

Figure S18: $^{13}$C NMR spectrum of p-OMe in CD$_3$CN at 294 K in the presence of the minor Z isomer.
Figure S19: $^1$H NMR spectrum of $p$-F in CD$_3$CN at 294 K in the presence of the minor Z isomer.

Figure S20: $^{13}$C NMR spectrum of $p$-F in CD$_3$CN at 294 K in the presence of the minor Z isomer.
Figure S21: $^1$H NMR spectrum of $p$-Cl in CD$_3$CN at 294 K in the presence of the minor Z isomer.

Figure S22: $^{13}$C NMR spectrum of $p$-Cl in CD$_3$CN at 294 K in the presence of the minor Z isomer.
Figure S23: $^1$H NMR spectrum of $p$-Br in CD$_3$CN at 294 K in the presence of the minor Z isomer.

Figure S24: $^{13}$C NMR spectrum of $p$-Br in CD$_3$CN at 294 K in the presence of the minor Z isomer.
Figure S25: $^1$H NMR spectrum of $p$-MC in CD$_3$CN at 294 K in the presence of the minor Z isomer.

Figure S26: $^{13}$C NMR spectrum of $p$-MC in CD$_3$CN at 294 K in the presence of the minor Z isomer.
Figure S27: $^1$H NMR spectrum of $p$-CN in CD$_3$CN at 294 K in the presence of the minor Z isomer.

Figure S28: $^{13}$C NMR spectrum of $p$-CN in CD$_3$CN at 294 K in the presence of the minor Z isomer.
Figure S29: $^1$H NMR spectrum of $p$-NO$_2$ in CD$_3$CN at 294 K in the presence of the minor Z isomer.

Figure S30: $^{13}$C NMR spectrum of $p$-NO$_2$ in CD$_3$CN at 294 K in the presence of the minor Z isomer.
References


