Supporting Information for

Kinetic Studies of Hantzsch Ester and Dihydrogen Donors Releasing Two Hydrogen Atoms in Acetonitrile

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SI. Syntheses of HEH$_2$ and 1(G)H$_2$-7(G)H$_2$

The syntheses of HEH$_2$ and 1(G)H$_2$-7(G)H$_2$ are shown below respectively. For the derivatives of 2(G)H$_2$-4(G)H$_2$, the syntheses are similar to the compound with no substituent. Benzaldehyde should be replaced by the corresponding substituents 4-G-benzaldehyde, other operations are consistent. The position of the substituents for 2(G)H$_2$-4(G)H$_2$ are also labeled as red “G”.

**Synthesis of HEH$_2$:**

\[
\begin{align*}
&\text{EtO}_2\text{C} \quad \text{EtO}_2\text{C} \\
&\text{H}_3\text{C} \quad \text{H}_3\text{C} \\
&\text{HCHO} \quad \text{HCHO} \\
&\text{NH}_3\text{H}_2\text{O} \quad \text{NH}_3\text{H}_2\text{O} \\
\end{align*}
\]

0.12 mol ethyl acetoacetate, 80 ml methanol, 0.06 mol formaldehyde and 0.06 mol NH$_3$•H$_2$O (25%) were added in 250 mL round bottom flask. The solution was refluxed for 8 h, and then the solution was cooled to room temperature. The precipitation was filtered and recrystallized from methanol to give HEH$_2$. The yield is 70%.

\[
\text{H NMR (CD}_3\text{CN, 400MHz): } \delta \text{ (ppm) 6.52 (s, 1H), 4.12 (q, 4H), 3.19 (s, 2H), 2.18 (s, 6H), 1.26 (t, 6H).}
\]

**Syntheses of 1(G)H$_2$:**

\[
\begin{align*}
&\text{GCHO} \\
&\text{NC} \quad \text{CN} \\
&\text{KOH} \\
&\text{HEH}_2, \text{MgClO}_4 \\
\end{align*}
\]

**Step a:**

Equimolar amounts of pure para-substituted benzaldehyde and malononitrile were dissolved in a minimum amount of 95% ethanol, a few drops of 10% potassium hydroxide solution were added. The resulted mixture was stirred at room temperature for 1 h, the product was precipitated and filtered to give olefin 1, and recrystallized with anhydrous ethanol. The yield is 78%.

**Step b:**

10 mmol olefin 1 was dissolved in dry acetonitrile, and 10.5 mmol HEH$_2$ was added, and adding a small amount of anhydrous Magnesium perchlorate as catalysis. The suspension was stirred well at room temperature. The mixture of the Product and dehydrogenation HE were obtained by silica gel column. The mixture was dissolved in anhydrous ether and washed successively with 1mol/L HCl, water, dried over MgSO$_4$, concentrated then dried to give the desired alkanes. The yield is 67%.

\[
\text{H NMR (CDCl}_3, \text{ 400MHz): } \delta \text{ (ppm) 3.21(d, 2H), 3.82(t, 1H), 3.79(s, 3H), 6.88-7.22(m, 4H).}
\]
$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 3.23 (d, 2H), 3.84 (t, 1H), 7.186-7.238 (d, 4H).

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 3.32 (d, 2H), 3.95 (t, 1H), 7.41 (m, 5H).

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 3.29 (d, 2H), 3.92 (t, 1H), 7.29-7.42 (d, 4H).

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 3.29 (d, 2H), 3.92 (t, 1H), 7.29-7.42 (d, 4H).

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 3.43 (d, 2H), 4.03 (t, 1H), 7.56-8.32 (d, 4H).

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 3.43 (d, 2H), 4.03 (t, 1H), 7.56-8.32 (d, 4H).

**Syntheses of 2(G)H$_2$:**

![Syntheses of 2(G)H$_2$](image)

**Step a:**

The benzaldehyde (10mmol) was added to the solution of indene 1,3-dione in ethanol, and a few drops of piperidine was added, then refluxed for 1 h, a yellow solid was obtained. Then cooled to room temperature, filtered, washed several times with ethanol and recrystallized in ethanol. The yield is 67%.

**Step b:**

0.02 mol sodium borohydride was slowly added to the solution of 0.01 mol olefins in ethanol. The mixture was maintained at 50-60°C for 15-20 minutes, then cooled to 0°C, and then slowly added 1 mol/L HCl. Then precipitated a white solid, vacuum filtration, recrystallized in methanol. The yield is 65%.

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 7.908 (m, 2H), 7.774 (m, 2H), 7.062 (d, 2H), 6.964 (d, 2H), 3.330 (s, 3H), 2.121 (s, 3H).

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 7.32 (m, 5H), 3.76 (t, 1H), 3.49 (d, 2H), 1.72 (s, 3H), 1.48 (s, 3H).

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 7.914 (m, 4H), 7.110 (s, 4H), 3.318 (s, 3H).
Syntheses of 3(G)H₂:

\[ \text{GCHO} + \text{O} \xrightarrow{\text{DMF, NaBH}_4, C_2H_5OH} \text{O} \xrightarrow{\text{HCl, C}_2\text{H}_5\text{OH}} \text{O} \]

**Step a:**
0.02 mol Meldrum acid and 0.02 mol benzaldehyde was dissolved in 15 mL DMF, the mixture was heated to 80°C, and held 1h, and then cooled to room temperature, the mixture was poured into 200 mL mixture of ice and water, then the solid appeared, filtered, washed with ice water, the crude product is purified by recrystallization in ethanol. The yield is 68%.

**Step b:**
0.02 mol sodium borohydride was slowly added to the solution of 0.01 mol olefins in 1 ethanol. The mixture was maintained at 50-60°C for 15-20 minutes, then cooled to 0°C, and then slowly added 1 mol/L HCl. Then precipitated a white solid, vacuum filtration, recrystallized in methanol. The yield is 74%.

**1H NMR (CDCl₃, 400MHz):**
- δ (ppm) 7.928 (t, 2H), 7.858 (t, 2H), 7.412 (d, 2H), 7.112 (d, 2H), 3.402 (s,3H).
- δ (ppm) 7.983 (d, 2H), 7.864 (d, 2H), 7.318 (d, 2H), 3.351 (s,3H).
- δ (ppm) 7.250 (d, 2H), 6.828 (d, 2H), 3.775 (s, 3H), 3.732 (t, 1H), 3.446 (d, 2H), 1.723 (s, 3H), 1.480 (s, 3H).
- δ (ppm) 7.210 (d, 2H), 7.101 (d, 2H), 3.452 (d, 2H), 2.300 (s, 3H), 1.722 (s, 3H), 1.491 (s, 3H).
- δ (ppm) 7.32 (m, 5H), 3.76 (t, 1H), 3.49 (d, 2H), 1.72 (s, 3H), 1.48 (s, 3H).
- δ (ppm) 7.355 (d, 2H), 7.301 (d, 2H), 3.758 (t, 1H), 3.498 (d, 2H), 1.752 (s, 3H), 1.521 (s, 3H).
- δ (ppm) 7.374 (d, 2H), 7.273 (d, 2H), 3.746 (t, 1H), 3.487 (d, 2H), 1.746 (s, 3H), 1.529 (s, 3H).
- δ (ppm) 7.721 (d, 2H), 7.327 (d, 2H), 3.842 (t, 1H), 3.552 (d, 2H), 1.729 (s, 3H), 1.496 (s, 3H).
Syntheses of $4(G)H_2$:

$$\text{CHO} + \text{O}_2 \text{N}_2 \text{O}_2 \text{G} \text{Zn} \text{CH}_3 \text{COOH}$$

**Step a:**

0.03 mol benzaldehyde and 0.03 mol barbituric acid was added to acetic acid, refluxed for 2 h. Then concentrated to 30 mL, cooled, a yellow solid was precipitated at room temperature by filtration, washed twice with cooled methanol. The yield is 68%.

**Step b:**

0.01 mol olefins was suspensioned in 150 mL glacial acetic acid, 6.4 g of zinc powder was added, then stirred at room temperature for 3 h. The gray suspension was filtered, the solid was washed three times with 20 mL acetic acid, the filtrate was concentrated under reduced pressure, and recrystallized in methanol. The yield is 70%.

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 7.25 (m, 3H), 7.03 (t, 2H), 3.78 (t, 1H), 3.46 (d, 2H), 3.12 (s, 6H).

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 7.25 (m, 3H), 7.03 (t, 2H), 3.78 (t, 1H), 3.46 (d, 2H), 3.12 (s, 6H).

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 7.25 (m, 3H), 7.03 (t, 2H), 3.78 (t, 1H), 3.46 (d, 2H), 3.12 (s, 6H).

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 7.220 (d, 2H), 7.019 (d, 2H), 3.778 (t, 1H), 3.460 (d, 2H), 3.170 (s, 6H).

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 7.373 (d, 2H), 6.965 (d, 2H), 3.779 (t, 1H), 3.447 (d, 2H), 3.174 (s, 6H).

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 7.513 (d, 2H), 7.241 (d, 2H), 3.824 (t, 1H), 3.551 (d, 2H), 3.206 (s, 6H).

Syntheses of $5(G)H_2$:

$$\text{NC} + \text{O}_2 \text{N}_2 \text{O}_2 \text{HEH}_2, \text{Mg(ClO}_4)_2 \text{NC}$$

**Step a:**

0.03 mol malononitrile and 0.03 mol acetophenone was dissolved in 20 mL toluene, 0.06 mol ammonium acetate and 2 mL of glacial acetic acid were added, the product of water was removed by the watershred. The residue was recrystallized in
ethanol. The yield is 65%.

**Step b:**

10 mmol olefin was dissolved in dry acetonitrile, and 10.5 mmol HEH$_2$ was added, and adding a small amount of anhydrous Magnesium perchlorate as catalysis. The suspension was stirred well at room temperature. The mixture of the Product and dehydrogenation HEH were obtained by silica gel column. The mixture was dissolved in anhydrous ether and washed successively with 1 mol/L HCl, water, dried over MgSO$_4$, concentrated then dried to give the desired alkanes. The yield is 60%.

$$\text{NC} \quad \text{CO}_2 \quad \text{Et}$$

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 7.790 (q, 4H), 7.517 (t, 2H), 7.413 (t,2H), 4.421 (d, 1H), 4.245 (d, 1H).

**Syntheses of 6H$_2$-7H$_2$:**

$$\text{NC} \quad \text{CO}_2 \quad \text{Et}$$

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) 7.784 (d, 2H), 7.568 (d, 1H), 7.496-7.429 (m, 3H), 7.372-7.317 (m, 2H), 4.629 (d, 1H), 4.293 (q, 2H), 4.185 (d, 1H).

**Step b:**

10 mmol olefin was dissolved in dry acetonitrile, and 10.5 mmol HEH was added, and adding a small amount of anhydrous Magnesium perchlorate as catalysis. The suspension was stirred well at room temperature. The mixture of the Product and dehydrogenation HEH$_2$ were obtained by silica gel column. The mixture was dissolved in anhydrous ether and washed successively with 1 mol/L HCl, water, dried over MgSO$_4$, concentrated then dried to give the desired alkanes. The yield is 60%.

$^1$H NMR(CDCl$_3$, 400MHz): $\delta$ (ppm) 7.752 (d, 2H), 7.563-7.426 (m, 4H), 7.310 (m, 2H), 4.552-4.466 (m, 4H), 1.495-1.482 (m, 6H).
SII. $^1$H NMR of the representative compounds

Some $^1$H NMR spectra of HEH$_2$ and 1(G)H$_2$-7(G)H$_2$ are shown below. Due to the large number of compounds involved in this paper, only several representative compounds' $^1$H NMR spectra are provided. And as HEH$_2$ and 1H$_2$-7H$_2$ have already been reported in literatures, they are identified only by $^1$H NMR spectra in this work.

Scheme S1. $^1$H NMR of HEH$_2$.

Scheme S2. $^1$H NMR of 1(CH$_3$)$_2$. 
Scheme S3. $^1$H NMR of 2(H)H$_2$.

Scheme S4. $^1$H NMR of 4(OCH$_3$)H$_2$. 
Scheme S5. $^1$H NMR of 3(CH$_3$)$_2$.

Scheme S6. $^1$H NMR of 1(H).
Scheme S7. $^1$H NMR of 4(H).
SIII. Products analysis for HAT reaction 4H$_2$/DPPH$^·$ by $^1$H NMR spectra

The products analysis for HAT reaction 4H$_2$/DPPH$^·$ are monitored by $^1$H NMR spectra (Scheme S8). Scheme S8(a) is $^1$H NMR spectra of DPPH$_2$, 4H$_2$ and the mixture of 4H$_2$ and DPPH$^·$. Scheme S8(b) is the enlarged drawing of $^1$H NMR spectra of the mixture of 4H$_2$ and DPPH$^·$. From Scheme S8(a), it can see that $\delta = 5.324$ ppm the nuclear magnetic peak of H on N-H in DPPH$_2$ appears at $\delta = 5.324$ ppm, indicating that hydrogen atom transfer reaction has taken place and DPPH$_2$ has been generated. From Scheme S8(b), the nuclear magnetic peak of H on N-CH$_3$ of olefin 4 appeared at $\delta = 3.380-3.392$ ppm, indicating that dihydrogen transfer reaction occurred and olefin 4 was generated. Based on the comparison of the peak of C-H in 4H$_2$ and N-CH$_3$ in olefin 4, it can be inferred that the yield of the reaction 4H$_2$/DPPH$^·$ is about 29%.

Scheme S8(a). $^1$H NMR spectra of DPPH$_2$, 4H$_2$ and the mixture of 4H$_2$ and DPPH$^·$.

Scheme S8(b). $^1$H NMR spectra of products analysis for HAT reaction 4H$_2$/DPPH$^·$. 
SIV. Thermodynamic analytic platforms for the reaction mechanisms of XH₂/DPPH⁺ in acetonitrile

The thermodynamic analytic platforms for the reaction mechanisms of XH₂/DPPH⁺ in acetonitrile are shown below. From Schemes S9-15, it can be seen that the first hydrogen (attached to polar group) transfer is the rate determining step when dihydrogen transfer occurs between XH₂ and DPPH⁺. Therefore, when comparing the dihydrogen donating ability of XH₂, the bond dissociation free energy ΔG°(XH₂), kinetic internal resistance energy ΔG°k(XH₂/XH⁺) and thermo-kinetic parameter ΔG°o(XH₂) of the first hydrogen leaving are only discussed in this work.

Scheme S9. Thermodynamic analytic platform (TAP) for the reaction mechanism of 1H₂ with DPPH⁺ in acetonitrile. Diagnostic conclusion from TAP: the most likely reaction pathway of 1H₂/DPPH⁺ is showed by red arrows: step 1 (rate-limited).
Scheme S10. Thermodynamic analytic platform (TAP) for the reaction mechanism of 2H₂ with DPPH⁻ in acetonitrile. Diagnostic conclusion from TAP: the most likely reaction pathway of 2H₂/DPPH⁻ is showed by red arrows: step 1 (rate-limited).

Scheme S11. Thermodynamic analytic platform (TAP) for the reaction mechanism of 3H₂ with DPPH⁻ in acetonitrile. Diagnostic conclusion from TAP: the most likely reaction pathway of 3H₂/DPPH⁻ is showed by red arrows: step 1 (rate-limited).
Scheme S12. Thermodynamic analytic platform (TAP) for the reaction mechanism of 4H₂ with DPPH⁺ in acetonitrile. Diagnostic conclusion from TAP: the most likely reaction pathway of 4H₂/DPPH⁺ is showed by red arrows: step 1 (rate-limited).

Scheme S13. Thermodynamic analytic platform (TAP) for the reaction mechanism of 5H₂ with DPPH⁺ in acetonitrile. Diagnostic conclusion from TAP: the most likely reaction pathway of 5H₂/DPPH⁺ is showed by red arrows: step 1 (rate-limited).
Scheme S14. Thermodynamic analytic platform (TAP) for the reaction mechanism of 6H₂ with DPPH• in acetonitrile. Diagnostic conclusion from TAP: the most likely reaction pathway of 6H₂/DPPH• is showed by red arrows: step 1 (rate-limited).

Scheme S15. Thermodynamic analytic platform (TAP) for the reaction mechanism of 7H₂ with DPPH• in acetonitrile. Diagnostic conclusion from TAP: the most likely reaction pathway of 7H₂/DPPH• is showed by red arrows: step 1 (rate-limited).
SV. Absorbance decays of 'Bu$_3$PhO' for HAT reactions HEH$_2$/'Bu$_3$PhO' and 3(CH$_3$)$_2$H$_2$/'Bu$_3$PhO' in acetonitrile at 298 K

The absorbance decay of 'Bu$_3$PhO' for HAT reactions HEH$_2$/'Bu$_3$PhO' and 3(CH$_3$)$_2$H$_2$/'Bu$_3$PhO' in acetonitrile at 298 K are shown below to supporting Table 3 in manuscript. According to the rate constants of these two reactions, it can be seen that the rate constants of HAT reactions can be predicted accurately by using the thermo-kinetic parameters of the dihydrogen donors and free radicals.

Figure S1. Decay of the 631 nm absorbance of 'Bu$_3$PhO' (1.0 mM) following the addition of HEH$_2$ (20 mM) in deaerated anhydrous acetonitrile at 298 K (black line) and the fit (red line) using pseudo-first-order kinetic model.

Figure S2. Decay of the 631 nm absorbance of 'Bu$_3$PhO' (1.0 mM) following the addition of 3(CH$_3$)$_2$H$_2$ (20 mM) in deaerated anhydrous acetonitrile at 298 K (black line) and the fit (red line) using pseudo-first-order kinetic model.