Supporting Information
for
Characterization of the synthetic cannabinoid

MDMB-CHMCZCA

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§Equal contributors
*Corresponding author

NMR spectra, UV and ECD spectra, IR and VCD spectra, HPLC/ESI-MS”, chiral HPLC, and computational chemistry
1 NMR Spectra

This section contains the NMR spectra of pure \((S)-3\) from test purchase 1 (internet shop, Dec 2015).
Figure 1.1: $^1$H NMR spectrum (600 MHz, CDCl$_3$) of 3.

Figure 1.2: $^{13}$C NMR spectrum (151 MHz, CDCl$_3$) of 3.
Figure 1.3: COSY spectrum (600 MHz, CDCl$_3$) of 3 (triethylammonium impurity marked with black boxes).

Figure 1.4: NOESY spectrum (600 MHz, CDCl$_3$) of 3.
Figure 1.5: HSQC spectrum (600 MHz, CDCl₃) of 3.

Figure 1.6: HMBC spectrum (600 MHz, CDCl₃) of 3.
Figure 1.7: \([^{1}H,^{15}N]\)-HSQC spectrum (600 MHz, CDCl\(_3\)) of 3.

Figure 1.8: \([^{1}H,^{15}N]\)-HMBC spectrum (600 MHz, CDCl\(_3\)) of 3.
2 UV and ECD Spectra

This section contains the UV and ECD spectra of pure \((S)\)-3 from test purchase 1 (internet shop, Dec 2015).

2.1 TD-B3LYP/6-311++G**/IEFPCM

![UV and ECD Spectra](image)

**Figure 2.1:** Observed (top) and calculated (bottom) UV spectra for \((S)\)-3 in MeCN.

![UV and ECD Spectra](image)

**Figure 2.2:** Observed (top) and calculated (bottom) ECD spectra for \((S)\)-3 in MeCN.

Fitting results: \(\sigma/\gamma = 0.27\) eV, \(s = 3\) nm, similarity UV: 0.9465, similarity ECD: 0.6473, similarity enantiomeric ECD: 0.3034, ESI: 0.3439.
2.2 TDA-B3LYP/6-311++G**/IEFPCM

![Graph](image1)

Figure 2.3: Observed (top) and calculated (bottom) UV spectra for (S)-3 in MeCN.

![Graph](image2)

Figure 2.4: Observed (top) and calculated (bottom) ECD spectra for (S)-3 in MeCN.

Fitting results: $\sigma/\gamma = 0.28 \text{ eV}$, $s = 11 \text{ nm}$, similarity UV: 0.9762, similarity ECD: 0.4830, similarity enantiomeric ECD: 0.4130, ESI: 0.0700.
2.3 TDA-RIJCOSX-B3LYP/def2-TZVPP/COSMO

Figure 2.5: Observed (top) and calculated (bottom) UV spectra for (S)-3 in MeCN.

Figure 2.6: Observed (top) and calculated (bottom) ECD spectra for (S)-3 in MeCN.

Fitting results: $\sigma/\gamma = 0.24 \text{ eV}, s = 14 \text{ nm}$, similarity UV: 0.9854, similarity ECD: 0.4137, similarity enantiomeric ECD: 0.5367, ESI: 0.1230 (inverted).
2.4 TDA-RIJCOSX-B3LYP/def2-TZVPP/SMD

![UV and ECD Spectra](image)

**Figure 2.7:** Observed (top) and calculated (bottom) UV spectra for (S)-3 in MeCN.

![Fitting results](image)

**Figure 2.8:** Observed (top) and calculated (bottom) ECD spectra for (S)-3 in MeCN.

Fitting results: $\sigma/\gamma = 0.26$ eV, $s = 16$ nm, similarity UV: 0.9833, similarity ECD: 0.2221, similarity enantiomeric ECD: 0.6548, ESI: 0.4327 (inverted).
2.5 TDA-RIJCOSX-B3LYP/ma-def2-TZVPP/COSMO

Figure 2.9: Observed (top) and calculated (bottom) UV spectra for (S)-3 in MeCN.

Figure 2.10: Observed (top) and calculated (bottom) ECD spectra for (S)-3 in MeCN.

Fitting results: $\sigma/\gamma = 0.22$ eV, $s = 11$ nm, similarity UV: 0.9871, similarity ECD: 0.4887, similarity enantiomeric ECD: 0.3950, ESI: 0.0937.
2.6 TDA-RIJCOSX-CAM-B3LYP/def2-TZVPP/COSMO

Figure 2.11: Observed (top) and calculated (bottom) UV spectra for (S)-3 in MeCN.

Figure 2.12: Observed (top) and calculated (bottom) ECD spectra for (S)-3 in MeCN.

Fitting results: $\sigma/\gamma = 0.25 \text{ eV}$, $s = 34 \text{ nm}$, similarity UV: 0.9589, similarity ECD: 0.3943, similarity enantiomeric ECD: 0.3910, ESI: 0.0033.
2.7 TD-CAM-B3LYP/def2-TZVPP/IEFPCM

![Graph showing UV and ECD spectra for (S)-3 in MeCN.]

**Figure 2.13:** Observed (top) and calculated (bottom) UV spectra for (S)-3 in MeCN.

![Graph showing observed and calculated ECD spectra for (S)-3 in MeCN.]

**Figure 2.14:** Observed (top) and calculated (bottom) ECD spectra for (S)-3 in MeCN.

Fitting results: $\sigma/\gamma = 0.29$ eV, $s = 24$ nm, similarity UV: 0.9431, similarity ECD: 0.3274, similarity enantiomeric ECD: 0.4607, ESI: 0.1333 (inverted).
2.8 TD-\(\omega\text{B97XD/def2-TZVPP/IEFPCM}\)

![UV and ECD Spectra](image)

**Figure 2.15:** Observed (top) and calculated (bottom) UV spectra for (S)-3 in MeCN.

![UV and ECD Spectra](image)

**Figure 2.16:** Observed (top) and calculated (bottom) ECD spectra for (S)-3 in MeCN.

Fitting results: \(\sigma/\gamma = 0.29\text{ eV}, s = 26\text{ nm},\) similarity UV: 0.9428, similarity ECD: 0.2600, similarity enantiomeric ECD: 0.4873, ESI: 0.2274 (inverted).
3 IR and VCD Spectra

This section contains the IR and VCD spectra of pure (S)-3 from test purchase 1 (internet shop, Dec 2015).

![IR and VCD Spectra](image)

**Figure 3.1:** Observed (top) and calculated (bottom) IR spectra for (S)-3 in CDCl₃.

![VCD Spectra](image)

**Figure 3.2:** Observed (top) and calculated (bottom) VCD spectra for pure (S)-3 in CDCl₃.

Fitting results: $\gamma = 8 \text{ cm}^{-1}$, $s = 0.982$, similarity IR: 0.9535, similarity VCD: 0.8263, similarity enantiomeric VCD: 0.0255, ESI: 0.8008.
4 Crystal Structure Determination

![Molecular structure of (S)-3 in the solid state (ORTEP-ellipsoids drawn at 30% probability, C: black, H: gray, N: blue, O: red).](image)

**Figure 4.1:** Molecular structure of (S)-3 in the solid state (ORTEP-ellipsoids drawn at 30% probability, C: black, H: gray, N: blue, O: red).

**Table 4.1:** Crystal structure determination of (S)-3.

<table>
<thead>
<tr>
<th>Crystal data:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>molecular formula</td>
<td>C$<em>{27}$H$</em>{34}$N$_2$O$_3$</td>
</tr>
<tr>
<td>molar mass</td>
<td>434.6 g mol$^{-1}$</td>
</tr>
<tr>
<td>crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>space group</td>
<td>$P2_12_12_1$</td>
</tr>
<tr>
<td>absorption coefficient ($\mu$)</td>
<td>0.62 mm$^{-1}$ (corrected with 6 crystal faces)</td>
</tr>
<tr>
<td>transmission</td>
<td>$T_{\text{min}} = 0.91, T_{\text{max}} = 0.98$</td>
</tr>
<tr>
<td>habitus</td>
<td>colorless needle</td>
</tr>
<tr>
<td>crystal size</td>
<td>0.04 $\times$ 0.05 $\times$ 0.2 mm$^3$</td>
</tr>
<tr>
<td>lattice constants (from 21059 reflections with 2.8° $&lt; \theta &lt; 68.1°$)</td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td>5.61656(18) Å</td>
</tr>
<tr>
<td>$b$</td>
<td>13.3920(5) Å</td>
</tr>
</tbody>
</table>
Crystal Structure Determination

\begin{align*}
c &= 31.5475(11) \text{Å} \\
V &= 2372.91(14) \text{Å}^3 \\
Z &= 4 \\
F(000) &= 936
\end{align*}

**temperature**

110 K

**density (calculated)**

1.216 g cm\(^{-3}\)

**Data collection:**

- **diffractometer:** STOE IPDS 2T
- **radiation:** Cu-\(K_\alpha\), \(\mu\)S mirror
- **scan type:** \(\omega\) scans
- **scan width:** 1\(^\circ\)
- **scan range:** 2\(^\circ\) \(\leq \theta \leq 68.2\(^\circ\)
  
  -6 \(\leq h \leq 6\)
  
  -16 \(\leq k \leq 16\)
  
  -37 \(\leq l \leq 24\)

**collected reflections:** 17495

**independent reflections:** 4263 (\(R_{int} = 0.033\))

**observed reflections:** 3283 (\(I/\sigma_I \geq 2\))

**Data correction, structure solution and refinement:**

- **corrections:** Lorentz and polarization correction
- **solution:** SHELXT-2014\(^{[1]}\)
- **refinement:** SHELXL-2014\(^{[2]}\) (full-matrix method); 317 refined parameters, weighted refinement:

\[
w = [\sigma^2(F_o^2) + (0.0975 \cdot P)^2 + 2.22 \cdot P]^{-1}
\]

with

\[
P = \frac{1}{3}[\max(F_o^2, 0) + 2 \cdot F_c^2];
\]

- hydrogen atoms generated with appropriate geometric constraints and allowed to ride on their respective parent atoms, NH localized and refined, non-hydrogen atoms anisotropically refined

**discrepancy factors**

\(wR_2 = 0.2109\)

\(R_1 = 0.0657\) (observed reflections)

\(R_1 = 0.0923\) (all reflections)

**goodness-of-fit (\(S\))**

1.121

**Flack parameter (\(x\))**

-0.069(136)

**maximum change of parameters**

0.001 \(\cdot\) esd

**maximum peak height in differential Fourier synthesis**

0.53 \(e \text{ Å}^{-3}\), -0.30 \(e \text{ Å}^{-3}\)

**comment**

ester oxygen atom and one methyl group are disordered
Figure 5.1: HPLC/ESI-MS of pure (S)-3 from test purchase 1 (internet shop, Dec 2015).
Figure 5.2: ESI-MS$^3$(435) of pure ($S$)-3 from test purchase 1 (internet shop, Dec 2015).
Figure 5.3: ESI-MS$^3$ (435→290) of pure (S)-3 from test purchase 1 (internet shop, Dec 2015).
Figure 5.4: ESI-MS$^4(435\rightarrow290\rightarrow280)$ of pure (S)-3 from test purchase 1 (internet shop, Dec 2015).
Figure 5.5: ESI-MS<sup>4</sup>(435→290→262) of pure (S)-3 from test purchase 1 (internet shop, Dec 2015).
Figure 5.6: ESI-MS$^4$(435→290→194) of pure (S)-3 from test purchase 1 (internet shop, Dec 2015).
Figure 5.7: HPLC/ESI-MS of (R/S)-3 after treatment of pure (S)-3 from test purchase 1 (internet shop, Dec 2015) with NaOMe/MeOH.
Figure 5.8: HPLC/ESI-MS of “pure” (S)-3 from test purchase 2 (internet shop, May 2016, contaminant: chloro-MDMB-CHMCZCA).
Figure 5.9: ESI-MS of chloro-MDMB-CHMCZCA contained as impurity in "pure" (S)-3 from test purchase 2 (internet shop, May 2016).
Figure 5.10: HPLC/ESI-MS of extracted (S)-3 from test purchase 3 (hashish-like resin, Jan 2016, contaminant: chloro-MDMB-CHMCZCA).
Figure 5.11: HPLC/ESI-MS of extracted (S)-3 from test purchase 4 (herbal mixture, Mar 2016).
Figure 5.12: HPLC/ESI-MS of extracted (S)-3 from test purchase 5 (herbal mixture, Mar 2016).
Figure 5.13: HPLC/ESI-MS of extracted (S)-3 from police seizure 1 (herbal mixture, Feb 2015, contaminant: chloro-MDMB-CHMCZCA).
Figure 5.14: HPLC/ESI-MS of extracted (S)-3 from police seizure 2 (herbal mixture, Feb 2015, contaminants: 5F-ADB/5F-MDMB-PINACA and MMB-CHMICA).
Figure 5.15: ESI-MS$^n$ of MMB-CHMICA contained as impurity in extracted ($S$)-3 from police seizure 2 (herbal mixture, Mar 2015).
Figure 5.16: HPLC/ESI-MS of extracted (S)-3 from police seizure 3 (herbal mixture, Aug 2016, contaminant: 5F-ADB/5F-MDMB-PINACA).
Figure 5.17: ESI-MS$^n$ of 5F-ADB/5F-MDMB-PINACA contained as impurity in extracted (S)-3 from police seizure 3 (herbal mixture, Aug 2016).
Figure 5.18: HPLC/ESI-MS of a blank sample.
6 Chiral HPLC

Figure 6.1: Chiral HPLC of \((R/S)\)-3.

Figure 6.2: Chiral HPLC of pure \((S)\)-3 from test purchase 1 (internet shop, Dec 2015).
Figure 6.3: Chiral HPLC of “pure” (S)-3 from test purchase 2 (internet shop, May 2016).

Figure 6.4: Chiral HPLC of extracted (S)-3 from test purchase 3 (hashish-like resin, Jan 2016).
Figure 6.5: Chiral HPLC of extracted (S)-3 from test purchase 4 (herbal mixture, Mar 2016).

Figure 6.6: Chiral HPLC of extracted (S)-3 from test purchase 5 (herbal mixture, Mar 2016).
Figure 6.7: Chiral HPLC of extracted (S)-3 from police seizure 1 (herbal mixture, Feb 2015).

Figure 6.8: Chiral HPLC of extracted (S)-3 from police seizure 2 (herbal mixture, Mar 2015).
Figure 6.9: Chiral HPLC of extracted (S)-3 from police seizure 3 (herbal mixture, Aug 2016).

Figure 6.10: Chiral HPLC of a blank sample.
7 Computational Chemistry

7.1 Keyword Lines

- conformational analysis using MMFF or PM6 (Spartan):
  ```
  SEARCHMETHOD=SPARSE FINDBOATS KEEPALL CONF_SELECTION_RULE=5
  ```

- semiempirical geometry optimization (Gaussian):
  ```
  #p opt=tight pm6
  ```

- DFT geometry optimization at double-\(\zeta\) level (Gaussian):
  ```
  #p opt=tight b3pw91 6-31g(d) scrf=(iefcpcm,solvent=chloroform) int=grid=ultrafine
  ```

- DFT geometry optimization and frequency analysis at triple-\(\zeta\) level in chloroform (Gaussian):
  ```
  #p opt=tight freq=vcd b3pw91 6-31g(d,p) scrf=(iefcpcm,solvent=chloroform)
  int=grid=ultrafine
  ```

- DFT geometry optimization and frequency analysis at triple-\(\zeta\) level in acetonitrile (Gaussian):
  ```
  #p opt=tight freq=vcd b3pw91 6-311g(d,p) scrf=(iefcpcm,solvent=acetonitrile)
  int=grid=ultrafine
  ```

- TD-DFT/TDA calculations (Gaussian):
  ```
  #p td(nstates=75,singlets) b3lyp 6-311++g(d,p) scrf=(iefcpcm,solvent=acetonitrile)
  int=grid=ultrafine
  ```

- TDA calculations (Orca):
  ```
  ! B3LYP def2-TZVPP def2-TZVPP/J RIJCOSX TightSCF Grid5 FinalGrid6 GridX4
  ! COSMO(acetonitrile)
  %tddft maxdim 600 nroots 100 end
  ! B3LYP def2-TZVPP def2-TZVPP/J RIJCOSX TightSCF Grid5 FinalGrid6 GridX4
  ! COSMO
  %cosmo smd true solvent "ACETONITRILE" end
  %tddft maxdim 600 nroots 100 end
  ! B3LYP ma-def2-TZVPP AutoAux RIJCOSX TightSCF Grid5 FinalGrid6 GridX4
  ! COSMO(acetonitrile)
  %tddft maxdim 600 nroots 100 end
  ! CAM-B3LYP def2-TZVPP def2-TZVPP/J RIJCOSX TightSCF Grid5 FinalGrid6 GridX4
  ! COSMO(acetonitrile)
  %tddft maxdim 600 nroots 100 end
  ```
## 7.2 Boltzmann Weightings

Table 7.1: Boltzmann Analysis for (S)-3 in chloroform.

<table>
<thead>
<tr>
<th>Conformer</th>
<th>$H/E_h$</th>
<th>$\Delta H$</th>
<th>$\Delta H$</th>
<th>Fraction</th>
<th>Boltzmann Factor</th>
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<tr>
<td>mmff-M5</td>
<td>-1383.842090</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.092</td>
<td>1.000</td>
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<td>mmff-M3</td>
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<td>0.1104</td>
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<td>0.830</td>
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<td>0.5592</td>
<td>0.1337</td>
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<tr>
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<td>0.080</td>
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<td>mmff-M20</td>
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</tr>
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In the following, the atomic coordinates for the optimized conformers of (-3)-3 in chloroform are given in xyz format:

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Figure 7.1: Lowest-energy conformer of (-3)-3 in chloroform.
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C -1.24784 1.66547 -0.16949
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C 1.00212 0.81394 -0.27974
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8 Bibliography
