NMR Data Repository

Oxidation-reduction and photophysical properties of isomeric forms of Safranin

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§NMR Plots and Assignments were originally done with an atom label scheme that was redone twice. The final conversion key is provided in the next page
New Green

Conversion Key

I:

1  2  3  4  5  6  7  8  9  10  11
N10+ 10a  1  2  3  4  4a  N5  5a  6  7
12  13  14  15  16  17  18  19  20  21  22
8   9   9a  2-NH2  8-NH2  3-CH3  9-CH3  F1  F2  F3  F4

II:

1  2  3  4  5  6  7  8  9  10  11
N10+ 10a  1  2  3  4  4a  N5  5a  6  7
12  13  14  15  16  17  18  19  20  21  22
8   9   9a  2-NH2  8-NH2  3-CH3  9-CH3  F1  F2  F3  F4

III:

1  2  3  4  5  6  7  8  9  10  11
N10+ 10a  1  2  3  4  4a  N5  5a  6  7
12  13  14  15  16  17  18  19  20  21  22
8   9   9a  2-NH2  8-NH2  3-CH3  6-CH3  F1  F2  F3  F4

IV:

1  2  3  4  5  6  7  8  9  10  11
N10+ 10a  1  2  3  4  4a  N5  5a  6  7
12  13  14  15  16  17  18  19  20  21  22
8   9   9a  2-NH2  8-NH2  3-CH3  6-CH3  F1  F2  F3  F4
Compound I
Overlay HSSQC (green) HMBC (blue) $^{13}$C
| Peak | v(F1) [ppm] | Intensity [abs] | Annotation |
|------|-------------|----------------|------------|
| 1    | 7.8662      | 108341.04      | \(f\ 7.858, d, H10\) |
| 2    | 7.8510      | 116460.55      | \(s, H6\) |
| 3    | 7.8170      | 152940.91      | \(s\) |
| 4    | 7.7599      | 135634.41      | \(f\ 7.760, m, H22\) |
| 5    | 7.7570      | 124597.31      | \(f\ 7.75, m, H21\) |
| 6    | 7.7511      | 256309.37      | \(f\ 7.67, m, H2+H20\) |
| 7    | 7.7485      | 274413.30      | \(broad, NH_2\) |
| 8    | 7.6727      | 151673.62      | \(f\ 7.328, d, H11\) |
| 9    | 7.6684      | 126621.58      | \(f\, NH_4+\) |
| 10   | 7.6659      | 111807.34      | \(s\, H3\) |
| 11   | 7.6598      | 132438.75      | \(s, H17(CH_3)\) |
| 12   | 7.6571      | 112099.86      | \(s, H18(CH_3)\) |
| 13   | 7.5489      | 31242.37       | \(N15\) |
| 14   | 7.3361      | 136008.72      | \(N1, 160.1 ppm\) |
| 15   | 7.3209      | 129056.82      | \(N8, 339.3 ppm\) |
| 16   | 7.1702      | 18784.16       | \(N15, 97.2 ppm\) |
| 17   | 6.0749      | 261753.79      | \(N16, 98.4 ppm\) |

N15 assignments (from N15-HMBC): 

- N1: 160.1 ppm
- N8: 339.3 ppm
- N15: 97.2 ppm
- N16: 98.4 ppm

NH_4+ Counter ion: 22.7 ppm
| Peak | v(F1) [ppm] | Intensity [abs] | Annotation |
|------|-------------|----------------|------------|
| 1    | 206.5402    | 96545.38      | acetone    |
| 2    | 157.7166    | 20370.16      | TFE-COO    |
| 3    | 157.1470    | 96684.19      | C12        |
| 4    | 156.7353    | 102063.88     | C4         |
| 5    | 140.0667    | 93138.53      | C19        |
| 6    | 136.7409    | 90213.75      | C2         |
| 7    | 136.4524    | 84922.62      | C9         |
| 8    | 135.0040    | 86223.09      | C7         |
| 9    | 134.4387    | 96492.12      | C14        |
| 10   | 132.3304    | 106964.50     | C10        |
| 11   | 131.9459    | 113155.00     | C6         |
| 12   | 130.4178    | 83802.72      | C22        |
| 13   | 130.2843    | 224186.88     | C20        |
| 14   | 129.1346    | 219948.84     | C20        |
| 15   | 129.0596    | 112665.56     | C5         |
| 16   | 120.9981    | 90892.34      | C11        |
| 17   | 101.1461    | 96349.72      | C13        |
| 18   | 94.0638     | 123458.56     | C3         |
| 19   | 30.6949     | 600818.94     | acetone    |
| 20   | 17.0508     | 193480.66     | C17        |
| 21   | 13.2311     | 200940.38     | C18        |
Compound II
Symmetric $\Rightarrow$ Final Compound II

Saft_peak3_Eskil_asrc800_20190429 2 1 /home/hsin/nmndata/bdata/eskil

- $\text{NH}_4^+$
- $\text{N15}$
- $\text{N1}$
- $\text{N8}$

$\text{N15}$ - HMBC

$\text{C}_{18}\text{H}_{19}\text{N}_4$
Saft_peak 3

C13- HSQC (green), HMBC (blue) - Region
| Peak | v(F1) [ppm] | Intensity [abs] | Annotation |
|------|-------------|----------------|------------|
| 1    | 158.3686    | 102167.34      | CF3COO-    |
| 2    | 158.1409    | 98418.94       | CF3COO-    |
| 3    | 156.2150    | 731377.09      | C4         |
| 4    | 136.4990    | 339893.06      | C19        |
| 5    | 135.4654    | 706146.88      | C7         |
| 6    | 135.2018    | 707764.28      | C2         |
| 7    | 131.7268    | 772086.00      | C6         |
| 8    | 131.4480    | 681200.66      | C21        |
| 9    | 130.8025    | 307922.97      | C22        |
| 10   | 129.0038    | 692971.59      | C5         |
| 11   | 127.6577    | 652229.00      | C20        |
| 12   | 117.4134    | 30232.59       | CF3        |
| 13   | 115.4503    | 27416.16       | CF3        |
| 14   | 93.5243     | 865726.31      | C3         |
| 15   | 17.2413     | 1460289.72     | C17        |
# Peak list data

| Peak | \( v(F1) \) [ppm] | Intensity [abs] | Annotation |
|------|--------------------|----------------|------------|
| 1    | 7.8743             | 1140833.05     | H21        |
| 2    | 7.8141             | 609189.80      | H22        |
| 3    | 7.7544             | 1945320.17     | H6         |
| 4    | 7.6183             | 1111930.53     | H20        |
| 5    | 7.6056             | 1051149.59     | H20        |
| 6    | 7.2567             | 140791.42      | NH4+       |
| 7    | 5.9297             | 2875198.02     | H3         |
| 8    | 2.2616             | 7150317.56     | H17        |

**N15 HMBC**

- N15: 95.2 ppm
- N1: 159.7 ppm
- N8: 336.5 ppm
- NH4+: 22.5 ppm
Compound III
This translation key is not the final version.

This compound was initially named 3, then 5 and back to III.
This component came out last in HPLC, i.e. least polar.

There are 4 ring protons. The adequate experiments indicate two of them are next to the NH₂-ring carbon. That model (A) clearly cannot be. The model is then revised as (B). All assignments then fall in place.

\[ \text{Diagram showing chemical structure with annotations} \]
The starting model was thought to be asymmetric. **Renamed to SaFT_peak25**

![Chemical Structure]

However, this N15-HMBC shows that Z of H1 can be connected to the N⁺ and NH₂.

So it seems to be inconsistent.
SaFT_peakS

`Saf0_peak3_EsKil_20180716.ascrc600 5 1 /home/hsin/nmrdata/bdata/esKil`
These are NH₄Cl peaks (see the last page).

HsQC detected 2 NH peaks peak at 23.0 ppm does not belong to the molecule, and not in exchange with H₂O, or other NH₂ group

One of the NH₂ group is detected at (7.74, 97.1 ppm), 'H is broadened (exchange with H₂O, NH₂)

The other NH₂ group is not detected (at 95 ppm) possibly corrected with an even broader peak at ~7.1 ppm
NOESY peaks between H2O and H(3&17) is consistent although sketchy.
This peak is on NH.

$\gamma_2 = 4.8 \text{ Hz}$

$\gamma_2 = 2.3 \text{ Hz}$

$\frac{1}{2}$

sharp

broad

$51.6 \text{ Hz}$

$12$

$21$

$20$

$22$

$4.5 \text{ Hz}$

$3$

$17$

$[\text{rel}]$

$[\text{ppm}]$

region
