

Supplementary Information

New Insights in the Photochromic

Spirodihydroindolizine/Betaine-System

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All chemicals were obtained from Acros Organics, unless noted otherwise. 400 MHz and 200 MHz Varian NMR-spectrometer and a Nicolet Protégé 460 FT-IR spectrometer were used in this study. We thank the Analytical Laboratory of Dr. Ruth Welti at KSU for recording the mass spectra of our compound employing an Applied Biosystems API-4000 triple quadrupole mass spectrometer with electrospray and APCI sources.

Fluorenone-9-hydrazone (2)

Hydrazine hydrate (6.024g, 0.12 mol of H₄N₂) was added drop-wise to a suspension of 9-fluorenone (20.0 g, 0.11 mol) in ethanol (200 ml) at RT. An exothermic reaction was observed, which subsided after 15 min. The reaction mixture was refluxed overnight and then allowed to cool down to RT. After 12 h, the precipitate (yellow needles) was separated by filtration and recrystallized from anhydrous ethanol. Yield: 15.5 g, 72.2%. The purity of compound (2) was confirmed by using TLC (silica, mobile phase: n-hexane/ethyl acetate 4/1 v/v, R_f=0.14).

Melting point 152 °C (reference 1: 152-153°C)

IR ν_{\max} (KBr pellets) cm⁻¹ 710, 773, 1198, 1449, 1577, 1600, 3060, 3201, 3313, 3385
1H-NMR (200 MHz, CDCl₃) δ_{H} 6.3 (2H s, -NH₂), 7.2-7.4 (4H m), 7.5-7.6 (1H dd, *J* 5.5 Hz, *J* 2.2 Hz), 7.6-7.7 (2H m), 7.9 (1H d, *J* 7 Hz)
13C-NMR (200MHz CDCl₃) δ_{C} 119.7, 120.6, 120.9, 125.6, 127.8, 128.1, 128.6, 129.8, 130.2, 138, 138.6 141.7 145.9

9-Diazofluorenone (3a)

A suspension of (2) (8.57g, 0.044 mol) in anhydrous diethyl ether (100 ml) was cooled to 0°C using an ice bath. Then, a thorough mixture of manganese dioxide (MnO₂, 10.2g, 0.117 mol, Aldrich) and anhydrous sodium sulfate (2.91g, 0.0205 mol, Fisher Scientific) was added in small amounts. The reaction mixture was allowed to warm up to RT during 30 min. Then, a mixture of 1.0 mL of saturated KOH in water and 25 mL of anhydrous ethanol was added at once and the reaction mixture stirred vigorously. (Note that it is important to wait until the KOH/H₂O mixture has cooled down to RT after mixing to avoid over-concentrating the KOH! The mixture was stirred at RT for 15h and filtrated. The solid phase was washed twice with 25 ml of anhydrous diethyl ether and then discarded. The combined liquid phases were concentrated to 60 ml and kept at 4°C overnight. The precipitate (red needles) of 9-diazofluorenone was filtered off, washed twice with (cold, 4°C) diethyl ether and then dried in high vacuum at RT. Yield: 8.11g, 95.0%.

Melting point 90 °C (dec.) (reference 2: 94-95°C)

IR ν_{\max} (KBr pellets) cm^{-1} 712.3, 743.1, 1229.5, 1326.8, 1372.9, 1439.5, 1600, 2069.4, 3032.1

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ_{H} 7.28- 7.38 (2H td, J 7.3 and 1.5 Hz), 7.37 (2H td, J 7.7 and 1.5 Hz), 7.5 (2H dt, J 7.7 and 0.7 Hz), 7.9 (2H dt, J 7.7 and 0.7 Hz)

$^{13}\text{C-NMR}$ (CDCl_3) δ_{C} 119.5, 121.1, 124.7, 126.5, 131.7, 133.2

1,2,4,5-Tetrazine, 3,6-dihydro-3,6-di-(spiro-1,9'-[9H]fluorene) (**3b**)

The filtrate contained a yellow compound (**3b**) (45 mg, 0.5%), which was separated by descending column chromatography (SiO_2 /ethyl acetate). Both, ^1H - and ^{13}C -NMR were very similar to compound (**3a**). Electrospray-MS indicated that this is the dimer of 9-diazofluorenone.

Melting point 89 °C (dec.)

IR ν_{\max} (KBr pellets) cm^{-1} 717.5, 748.2, 1425, 1650, 2059, 2331, 2356.1, 2842.6, 2924.6, 3042.39

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ_{H} 7.30 (2H td, J 7.7 and 1.4 Hz, 2H), 7.37 (2H td, J 7.7 and 1.4 Hz), 7.50 (2H dd, J 7.7 and 1 Hz), 7.93 (2H dt J 7.4 and 0.7 Hz)

$^{13}\text{C-NMR}$ (200 MHz, CDCl_3) δ_{C} 119.5 121.1 124.7, 126.5, 131.6, 133.1, 152.5

MS: $\text{C}_{26}\text{H}_{16}\text{N}_4$ m/z 384.5

Spiro[9H-fluorene-9,3'-[3H]pyrazole]-4',5'-dicarboxylic acid, dimethyl ester (**4**)

A solution of (**3a**) (5.07g, 0.026 mol) in 75mL of anhydrous diethyl ether was cooled to 0°C using an ice bath. Then a solution of 2-butynedioic acid dimethyl ester in 30 ml of anhydrous diethyl ether was added drop-wise to the continuously stirred solution. After all 2-butynedioic acid dimethyl ester was added, the ice bath was removed and the reaction mixture was allowed to stir for 24h. The yellow reaction mixture was concentrated to the half of its original volume and kept at 4°C overnight. Yellow crystals were obtained, separated from the mother liquor by filtration, and recrystallized from diethyl ether/ethanol (1:1 v/v). Yield: 6.59g, 74.8%

Melting point (dec.): 107-108 °C (reference 3: 114-117°C)

IR ν_{\max} (KBr pellets) cm^{-1} 748.2, 1147.6, 1250.07, 1316.6, 1434.4, 1639.2, 1741.68, 2945.09, 2990.0, 3062.8

$^1\text{H-NMR}$ δ_{H} (400 MHz, CDCl_3) δ_{H} 3.5 (3H s, $-\text{CO}_2\text{Me}$), 4.09 (3H s, $-\text{CO}_2\text{Me}$), 6.83 (2H dt, J 7.1 and 0.8 Hz), 7.27 (2H td, J 7.5 and 1.1 Hz), 7.49 (2H td, J 7.5 and 1.1 Hz), 7.8 (2H d, J 7.3 Hz)

$^{13}\text{C-NMR}$ ^{13}C (400 MHz, CDCl_3) δ_{C} 53.2, 53.4, 66, 121.4, 124.06, 128.5, 130.7, 132.8, 143.8, 149, 160.5, 162

MS $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_4$ m/z 335.2 and 357.1 (M+1 and M+Na)

Spiro[2-cyclopropene-1,9'-[9H]fluorene]-2,3-dicarboxylic acid, 2,3-dimethyl ester (**5**)

In a photochemical bench reactor, (**4**) (3.9g, 0.012 mol) in 350 ml of anhydrous diethyl ether was purged with N_2 for 30min and then irradiated employing a mercury medium pressure lamp (Hanovia 150W (608A0360)). N_2 was released vigorously at the beginning of the irradiation. The formation of bubbles stopped after 2.5h. A TLC check (SiO_2 , hexane/ethyl acetate, 3/1, v/v) confirmed that (**4**) had indeed completely

reacted. The yellow solution was then concentrated to one third of its original volume and kept overnight at 4°C. Yellow needles of pure compound (**5**) were obtained. Yield: 3.57g, 100%

Melting point: 147-149 °C (dec.) (reference 4: 149°C)

IR ν_{\max} (KBr pellets) cm^{-1} 737.9, 1050.3, 1250, 1429.3, 1721.1, 1854.34, 2950.21, 3073.1

¹H-NMR (400 MHz, CDCl₃) δ_{H} 3.83 (6H, s, 2-CO₂Me), 7.26 (2H d, *J* 7 Hz), 7.34 (2H td, *J* 7.3 and 0.7 Hz), 7.4 (2H td, *J* 7.4 and 1.1Hz), 7.8 (2H d, *J* 7.3 Hz)

¹³C-NMR (400 MHz, CDCl₃) δ_{C} 53.3, 120.3, 121.07, 121.6, 127.3, 128.1, 141.7, 144.5, 158.3

MS C₁₉H₁₄O₄ 307.1 and 329.2(M+1 and M+ Na)

Spiro[9H-fluorene-9,1'(8'aH)-indolizine]-2',3'-dicarboxylic acid, dimethyl ester (**7**)

The spirene (**5**), (0.50g, 0.0016 mol) was dissolved in 50 ml of anhydrous diethyl ether (dried over CaH₂ and distilled prior to use) at RT. A solution of pyridine (dried over KOH and distilled prior to use) (0.1266g, 0.0016 mol) in 5.0 ml of anhydrous diethyl ether was added drop-wise under vigorous stirring. The color of the mixture changed from light yellow to deep blue-green upon addition of pyridine indicating the formation of the betaine. The reaction mixture was continuously stirred in the dark at RT for 20h. TLC-control was used to check for the presence of non-reacted spirene (silica, n-hexane/ethyl acetate, 4/1, v/v). In the case that unreacted spirene was found, pyridine in diethyl ether (see above) was added (rate: 1 drop/h) and the reaction mixture was repeatedly checked by TLC until no more spirene was present. The volume of the reaction was decreased to 25 percent using a rotavap and the kept at 4°C overnight. Yellow crystals, which turn to green under irradiation and back to yellow in the dark, were obtained. Traces of pyridine were removed in high vacuum. Yield: 574 mg, 93%. Note that NMR indicates a quantitative reaction. The observed losses are caused by the crystallization procedure.

Melting point: 133-134 °C (reference 5: 132-133°C)

IR ν_{\max} (KBr pellets) cm^{-1} 743.1, 1122.05, 1224.4, 1255.1, 1444.6, 1552.2, 1588.05, 1675.1, 1746.8, 2786.34, 2945.05, 3032.15

¹H-NMR (400 MHz, CDCl₃) δ_{H} 3.25 (3H s), 3.98 (3H s), 4.4 (1H d, *J* 9.8 Hz), 5.1 (1H t, *J* 6.6 Hz), 5.4 (1H s), 5.64 – 5.69 (1H m), 6.4 (1H d, *J* 7.4), 7.2 (1H td, *J* 7.4 and 1 Hz), 7.28 – 7.39 (3H m), 7.4 (1H d, *J* 7.4 Hz), 7.5 (1H d, *J* 7.6 Hz), 7.7 (2H dd, *J* 7.4 and 0.8 Hz)

¹³C-NMR (400 MHz, CDCl₃) δ_{C} 51.1, 53.4, 68.8, 69.9, 104.8, 117.7, 119.8, 120.1, 123.4, 123.6, 124.6, 124.8, 127.2, 127.7, 128.2, 128.4, 141.8, 142.5, 160.5, 164.1

MS C₂₄H₁₉NO₄ *m/z* 384.3, 385.3, 386.2 (M-1, M+, M+1)

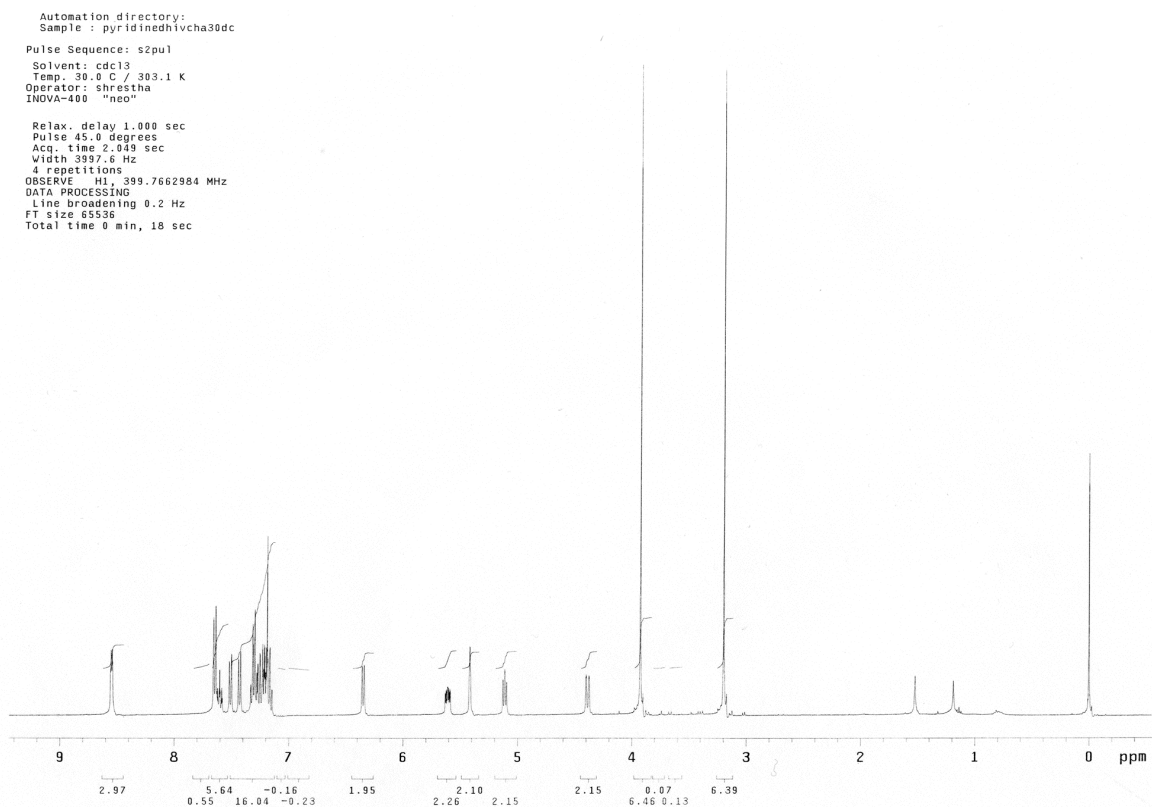


Figure 1: $^1\text{H-NMR}$ of Spiro[9H-fluorene-9,1'(8'aH)-indolizine]-2',3'-dicarboxylic acid, dimethyl ester (**7**)

References

1. H. Heydt, Product class 21: diazo compounds., *Science of Synthesis*, 2004, **27**, 843-935.
2. L. J. McDowell, M. M. Khodaei, D. Bethell, The decomposition of diazo-compounds induced by nucleophiles. The decomposition of 9-diazofluorene in the presence of hydroxide or alkoxide ions., *Organic & Biomolecular Chemistry*, 2003, **1**, 995-1003.
3. H. Duerr, H. Kober, R. Sergio, V. Formacek, NMR spectroscopic studies. 3. Pulse Fourier transform carbon-13 NMR and mass spectra of heterocyclics. 1,2-Diazaspiro[4.4]nonatetraenes, azaindolizines, and 3aH-indazoles., *Chemische Berichte*, 1974, **107**, 2037-49.
4. S. Mataka, M. Tashiro, Thermolysis of dimethyl 3,3-(2,2'-biphenyl)-3H-pyrazole-4,5-dicarboxylate., *J. Org. Chem.*, 1981, **46**, 1929-31.
5. H. Duerr, G. Hauck, Photochromic spiro[1,8-a-dihydroindolizines] and their use in radiation-sensitive materials., *Ger. Offen.*, 1980, **DE 2906193**, 29pp.