Electron-Rich Phenothiazine Congeners and Beyond: Synthesis and Electronic Properties of Isomeric Dithieno[1,4]thiazines

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1 General Considerations

All reactions were carried out in flame-dried Schlenk tubes by using syringes under nitrogen atmosphere. Dry solvents for reactions and analytics were directly used from a MB-SPS 800 solvent drying system (MBraun) except of toluene, which was refluxed under nitrogen atmosphere over sodium, distilled and stored in a Schlenk flask over molecular sieve 4 Å under nitrogen atmosphere. 10-Phenyl-10H-phenothiazine (1)\(^{[1]}\) and 4-phenyl-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (2a)\(^{[2]}\) and were synthesized according to the literature procedures as indicated. Commercial grade reagents were purchased from Sigma Aldrich, Alfa Aesar, ABCR, Fluorochem and ACROS and used as supplied without further purification. Crude mixtures were adsorbed on Celite® 545 (0.02–0.20 mm) from Carl Roth GmbH Co.KG. The purification of products was performed on silica gel 60 M (0.04–0.063 mm) from Macherey-Nagel by using the flash technique under a pressure of 2 bar. For TLC silica gel coated aluminium plates (60, F\(_{254}\)) from Merck were employed and analyzed with UV light at 254 or 365 nm.

\(^{1}\)H, \(^{13}\)C, and 135-DEPT NMR spectra were recorded at 293 K on 300 MHz (Bruker AVIII 300), 500 MHz (Bruker Avance DRX 500) and the resonances of the residues of non-deuterated CDCl\(_3\) (\(^{1}\)H \(\delta = 7.26\) ppm, \(^{13}\)C \(\delta = 77.00\) ppm), acetone-d\(_6\) (\(^{1}\)H \(\delta = 2.05\) ppm, \(^{13}\)C \(\delta = 29.84\) ppm) or THF-d\(_8\) (\(^{1}\)H \(\delta = 3.58\) ppm, \(^{13}\)C \(\delta = 67.57\) ppm) were locked as internal standards. The multiplicities of signals are abbreviated as follows: d = doublet, dd = doublet of doublets and m = multiplet. The assignments of C\(_{quat}\) and CH nuclei are based on DEPT spectra.

IR spectra were recorded on a Shimadzu IR Affinity-1 with ATR technique. The intensities of IR signals are abbreviated as s (strong), m (medium) and w (weak).

EI mass spectra were recorded on Triple-Quadrupole mass spectrometer TSQ 7000 (Finnigan MAT). MALDI-TOF mass spectra were measured on an UltrafleXtreme apparatus (Bruker Daltonics).

The elemental analyses were carried out on a Perkin Elmer Series II Analyser 2400 at the Institute for Pharmaceutical and Medicinal Chemistry at Heinrich-Heine-University Düsseldorf.

Melting points (uncorrected) were measured with a Büchi B545 apparatus.

Absorption spectra were recorded in dichloromethane high performance liquid chromatography (HPLC) grade at 293 K on Perkin Elmer UV/vis/NIR Lambda 19 spectrometer. For the determination of the extinction coefficients \(\varepsilon\), absorption measurements at five different concentrations were carried out. Emission spectra were recorded in dichloromethane HPLC grade at 293 K on a Perkin Elmer LS55 spectrometer.

Quantum chemical calculations were carried out utilizing the HPC-Cluster Ivybridge of the
Zentrum for Informations- und Medientechnologie (ZIM) at the Heinrich-Heine-University Düsseldorf.

Cyclic voltammetry experiments (EG&G Princeton Applied Research Model 263A potentiostat) were performed under argon atmosphere in dry and degassed dichloromethane at 293 K using n-Bu4NPF6 (0.1 M) as electrolyte and at scan rates v of 100, 250, 500 and 1000 mVs⁻¹. The three-electrode array consists of a working electrode with a 2 mm platinum disk, a platinum wire counter electrode, and an Ag/AgCl (3.0 M NaCl) reference electrode. The potentials were corrected by adding the internal standard decamethylferrocene to each measurement. Decamethylferrocene was referenced to the internal redox standard ferrocene (\(E^0_{0/+1}(\text{deca-methylferrocene}) = -95 \text{ mV vs. } E^0_{0/+1}(\text{ferrocene}) = 450 \text{ mV}\)).\[^3\] Therefore the outlined potentials are indirectly referenced to ferrocene.

2 Syntheses

2.1 One-pot synthesis of bis(4-bromothiophen-3-yl)sulfane (3a)\[^4\]

\[
\begin{align*}
\text{Br} & \quad \text{S} \quad \text{S} \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

In a flame-dried Schlenk vessel under nitrogen atmosphere were filled 829 mg (3.43 mmol, 1.00 equiv) 3,4-dibromothiophene (5b) and 4 mL dry diethyl ether and were cooled down to -78 °C (isopropanol/dry ice bath). Then, 2.14 mL (3.43 mmol, 1.00 equiv, 1.6 M in hexane) n-butyllithium was added dropwise slowly and the reaction solution was stirred for 15 min at -78 °C. The temperature was raised to 0 °C (water/ice bath) and the volatiles were removed in vacuo carefully (approx. 1 h). The remaining colorless solid was dissolved in 10 mL dry diethyl ether and was cooled down to -78 °C again. Next, 110 mg (3.43 mmol, 1.00 equiv) fine mortared sulfur was added and the stirring was continued for 15 min at -78 °C. Afterwards, while the temperature was raised to 0 °C, the stirring was continued for another 15 min. In the next step, 654 mg (3.43 mmol, 1.00 equiv) p-toluenesulfonyl chloride was added slowly. It was stirred vigorously for 10 min at 0 °C and then for 2 h at 40 °C. Simultaneously, 580 µL (4.12 mmol, 1.20 equivs) diisopropyl amine and 4 mL dry diethyl ether were charged into another flame-dried Schlenk vessel under nitrogen atmosphere and were cooled down to 0 °C. Then, 2.58 mL (4.12 mmol, 1.20 equivs, 1.6 M in hexane) n-butyllithium was added dropwise slowly to the diisopropyl amine solution. It was stirred for 10 min at 0 °C and for 10 min at ambient temperature after that. In the meantime, 671 mg (4.12 mmol, 1.20 equivs) 3-bromothiophene (5a) and 4 mL dry diethyl were filled into a third flame-dried Schlenk vessel under nitrogen atmosphere and were cooled down to -78 °C. The previously prepared lithium diisopropylamide solution was dropped into the 3-bromo-
thiophene solution and it was stirred at -78 °C for 30 min. This lithiated 3-bromothiophene was added to the vigorously stirred reaction solution, which had been cooled down to -78 °C before. Then, the reaction solution was stirred at -78 °C for 1.5 h. Finally, the reaction was quenched by the addition of 10 mL water. The organic layer was separated, the aqueous layer was extracted with diethyl ether three times and the combined organic layers were dried with dry magnesium sulfate. The volatiles were removed by evaporation and the crude product was purified chromatographically on silica gel (n-hexane) to give 488 mg (1.37 mmol, 40%) of 3a in form of a light-yellow oil.

R_f (n-hexane) = 0.50. 1H NMR (300 MHz, acetone-d_6): δ 7.18 (d, 3J_HH = 5.56 Hz, 1H), 7.39 (d, 5J_HH = 3.44 Hz, 1H), 7.70 (d, 5J_HH = 3.44 Hz, 1H), 7.75 (d, 3J_HH = 5.59 Hz, 1H). 13C NMR (75 MHz, Acetone-d_6): δ 113.1 (C_quat), 118.6 (C_quat), 126.3 (CH), 128.1 (CH), 131.8 (C_quat), 131.95 (CH), 132.03 (CH), 132.2 (C_quat). MS(EI) m/z (%): 358 ([81Br81Br-M]+, 16), 356 ([79Br81Br-M]+, 27), 354 ([79Br79Br-M]+, 15), 198 (14), 197 (13), 196 ([M – 2 Br]+, 100), 152 (10), 114 (14), 98 (12), 82 (22), 81 (13), 69 (27), 45 (12). IR: ν [cm⁻¹] = 3103 (w), 2922 (w), 2851 (w), 1699 (w), 1485 (m), 1472 (m), 1385 (w), 1342 (m), 1319 (m), 1246 (w), 1152 (m), 1113 (w), 1086 (w), 1024 (w), 1011 (w), 920 (m), 858 (s), 791 (s), 777 (s), 716 (s), 667 (m), 635 (w).

2.2 General procedure 1 (GP1) for the one-pot synthesis of dithienyl sulfides 3b and 3c

In a flame-dried Schlenk vessel under nitrogen atmosphere were filled 1.00 equiv of a bromothiophene 5 and 0.4 mL/mmol dry diethyl ether. The reaction solution was cooled down to -78 °C (isopropanol/dry ice bath). Then, 1.00 equiv n-butyllithium (1.6 M in hexane) was added dropwise slowly and the reaction solution was stirred for 30 min at -78 °C. The temperature was raised to 0 °C (water/ice bath) and the volatiles were removed in vacuo carefully (approx. 1 h). The remaining colorless to light yellow solid was dissolved in 0.4 mL/mmol dry diethyl ether and cooled down to -78 °C again. Next, 1.00 equiv fine mortared sulfur was added. The reaction solution had been stirred for 30 min at -78 °C and for 30 min at 0 °C afterwards. To the reaction solution was added 1.00 equivs p-toluenesulfonyl chloride slowly. It was stirred for 30 min at 0 °C and then for 3 h at 40 °C. Simultaneously, another portion of a bromothiophene 5 was lithiated: In a flame-dried Schlenk vessel under nitrogen atmosphere were filled 1.20 equivs of bromothiophene 5 and 0.4 mL/mmol dry diethyl ether. The reaction solution was cooled down to -78 °C. Then, 1.20 equivs n-butyllithium (1.6 M in hexane) were added dropwise slowly and the reaction solution was stirred for 30 min at -78 °C. Likewise, the volatiles were removed and the remaining colorless to light yellow solid was dissolved in 0.4 mL/mmol dry diethyl ether and
cooled down to -78 °C again. The resulting second portion of thienyl lithium was dropped to the reaction solution, which had been cooled down to -78 °C after the completion of the tosylation. The reaction solution was stirred overnight and was allowed to come to ambient temperature slowly meanwhile. The reaction was quenched by the addition of 50 mL water. The organic layer was separated, the aqueous layer was extracted with diethyl ether three times and the combined organic layers were dried with dry magnesium sulfate. The volatiles were removed by evaporation and the crude product was purified by column chromatography. For experimental details see table 1.

### Table 1. Experimental details GP 1.

| Bromo thiophene 5  | n-BuLi | S₈ | pTsCl | Yield 3 |
|--------------------|--------|----|-------|---------|
| [g] (mmol)         | [mL] (mmol) | [g] (mmol) | [g] (mmol) | [g] (%) |
| 3-Bromo thiophene (5a) | 3.261 (20.00)³ | 12.50 (20.00)³ | 0.641 (20.00) | 3.813 (20.00) | 3.018 (76) |
| 3.913 (24.00)³    | 15.00 (24.00)³ |
| 3,4-Dibromo thiophene (5b) | 2.42 (10.0)³ | 6.26 (10.0)³ | 0.321 (10.0) | 1.90 (10.0) | 5.61 (56) |
| 2.95 (12.2)³      | 7.62 (12.2)³ |

³a: 1st portion; b: 2nd portion; c: 1.6 M in hexane).

#### 2.2.1 Di(thiophen-3-yl)sulfane (3b)⁴

![Di(thiophen-3-yl)sulfane (3b)]

The crude product was synthesized following GP1 and purified chromatographically on silica gel (n-hexane) to give 3.018 g (15.22 mmol, 76 %) of 3b in form of a light-yellow oil.

Rᶠ(n-hexane) = 0.44. ¹H NMR (300 MHz, CDCl₃): ²δ 7.00 (dd, ³³J_HH = 5.03 Hz, ⁴³J_HH = 1.28 Hz, 2H), 7.19 (dd, ⁵³J_HH = 3.05 Hz, ⁶³J_HH = 1.30 Hz, 2H), 7.32 (dd, ⁷³J_HH = 5.01 Hz, ⁸³J_HH = 3.04 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 124.9 (CH), 126.6 (CH), 129.9 (CH), 131.6 (C_quat). MS (EI) m/z (%): 199 ([M + H]⁺, 13), 198 ([M]⁺, 100), 167 (13), 166 (10), 165 (13), 153 (48), 134 (10), 121 (19), 115 ([M – C₅H₅S]⁺, 7), 71 (14). IR: ν [cm⁻¹] = 1350 (m), 1196 (m), 1096 (m), 891 (m), 851 (m), 758 (s), 689 (m), 610 (m).
2.2.2 Bis(4-bromothiophen-3-yl)sulfane (3c)[4]

![Chemical structure of 3c](image)

The crude product was synthesized following GP1 and purified chromatographically on silica gel (n-hexane) to give 1.998 g (5.610 mmol, 56%) of 3c in form of a colorless oil.

Rf (n-hexane) = 0.43. ¹H NMR (300 MHz, acetone-d₆): δ 7.41 (d, J HH = 3.43 Hz, 2H), 7.71 (d, J HH = 3.45 Hz, 2H). ¹³C NMR (75 MHz, acetone-d₆): δ 114.0 (C quat), 126.2 (CH), 128.7 (CH), 131.7 (C quat). MS (EI) m/z (%): 358 ([2⁸¹Br-M]+, 9), 356 ([⁷⁹Br⁸¹Br-M]+, 16), 354 ([2⁷⁹Br-M]+, 8), 277 ([⁸¹Br-M – Br]+, 6), 275 ([⁷⁹Br-M – Br]+, 5), 198 (13), 197 (15), 196 ([M – 2 Br]+, 100), 98 (13), 82 (16), 81 (11), 69 (20). IR: ν [cm⁻¹] = 3103 (w), 1472 (m), 1454 (w), 1315 (s), 1260 (w), 1229 (w), 1198 (w), 1155 (w), 1111 (w), 1092 (w), 1064 (w), 1040 (w), 1015 (w), 920 (m), 880 (w), 849 (m), 791 (s), 773 (s), 746 (w), 719 (w), 698 (w), 658 (m), 635 (w).

2.3 One-pot synthesis of bis(3-bromothiophen-2-yl)sulfane (3d)[4]

![Chemical structure of 3d](image)

In a flame-dried Schlenk vessel under nitrogen atmosphere were filled 2.30 mL (16.3 mmol, 1.00 equiv) diisopropyl amine and 8 mL dry diethyl ether and cooled down to 0 °C (water/ice bath). Then, 10.2 mL (16.3 mmol, 1.00 equiv, 1.6 M in hexane) n-butyllithium was added dropwise slowly and the reaction solution was stirred for 10 min at 0 °C and for 10 min at ambient temperature after that. In the meantime, 2.65 g (16.3 mmol, 1.00 equiv) 3-bromothiophene (5a) and 16 mL dry diethyl ether were charged into another flame-dried Schlenk vessel under nitrogen atmosphere and cooled down to -78 °C (isopropanol/dry ice bath). The previously prepared lithium disopropylamide solution was dropped into the 3-bromothiophene solution. The reaction solution was stirred at -78 °C for 1 h. Next, 521 mg (16.3 mmol, 1.00 equiv) fine mortared sulfur was added and the stirring was continued for 15 min at -78 °C. While the temperature was raised to 0 °C, the stirring was continued for 1 h. In the next step, 3.10 g (16.3 mmol, 1.00 equiv) p-toluenesulfonyl chloride was added slowly. It was stirred vigorously for 15 min at 0 °C and then for 2 h at 40 °C. Simultaneously, another portion of 3-bromothiophene (5a) was lithiated as before: In a third flame-dried Schlenk vessel under nitrogen atmosphere were filled 2.70 mL (19.1 mmol, 1.00 equiv)
diisopropyl amine and 9 mL dry diethyl ether and cooled down to 0 °C. Then, 11.9 mL (19.0 mmol, 1.00 equiv, 1.6 M in hexane) n-butyllithium was added dropwise slowly. It was stirred for 10 min at 0 °C and for 10 min at ambient temperature after that. In the meantime, 3.12 g (19.1 mmol, 1.20 equivs) 3-bromothiophene (5a) and 19 mL dry diethyl ether were charged into a fourth flame-dried Schlenk vessel under nitrogen atmosphere and cooled down to -78 °C. The lithium diisopropylamide solution was dropped into the 3-bromothiophene solution and it was stirred at -78 °C for 1 h. This second portion of lithiated 3-bromothiophene was added to the vigorously stirred reaction solution, which had been cooled down to -78 °C before. The reaction solution was stirred at -78 °C for 2 h. Finally, the reaction was quenched by the addition of 25 mL water. The organic layer was separated, the aqueous layer was extracted with diethyl ether three times and the combined organic layers were dried with dry magnesium sulfate. The volatiles were removed by evaporation and the crude product was purified chromatographically on silica gel (n-hexane) and by recrystallization from n-hexane to give 2.56 g (8.30 mmol, 51%) of 3d in form of a colorless solid.

Mp.: 55–56 °C, Rf (n-hexane) = 0.30. 1H NMR (300 MHz, CDCl3): δ 7.00 (d, 3JHH = 5.54 Hz, 2H), 7.34 (d, 3JHH = 5.55 Hz, 2H). 13C NMR (75 MHz, CDCl3): δ 118.1 (Cquat), 129.99 (CH), 130.0 (Cquat), 131.0 (CH). MS(EI) m/z (%): 358 ([81Br81Br-M]+, 14), 356 ([79Br81Br-M]+, 24), 354 ([79Br79Br-M]+, 11), 198 (14), 196 ([M – 2 Br]+, 100). IR: ν [cm⁻¹] = 3094 (w), 3080 (w), 2922 (w), 1776 (w), 1732 (w), 1607 (w), 1582 (w), 1562 (w), 1512 (w), 1507 (w), 1512 (w), 1479 (w), 1445 (w), 1379 (m), 1341 (m), 1283 (w), 1175 (w), 1153 (m), 1084 (m), 1024 (w), 986 (w), 883 (w), 856 (s), 812 (w), 799 (w), 758 (w), 733 (s), 716 (s), 694 (m), 673 (w), 664 (w), 648 (w).

2.4 Bis(2-iodothiophen-3-yl)sulfane (3e)

In a Schlenk vessel under nitrogen atmosphere were charged 191 mg (0.960 mmol, 1.00 equiv) di(thiophen-3-yl)sulfane (5b) and 6 mL dry DMF and cooled down to 0 °C (water/ice bath). Then, 432 mg (1.92 mmol, 2.00 equivs) N-iodosuccinimide was added in one portion. The reaction solution was stirred for 46 h, while the temperature was raised to ambient temperature slowly by thawing. The reaction was quenched by the addition of 10 mL of a saturated sodium sulfite solution. The organic layer was separated, the aqueous layer was extracted with diethyl ether three times and the combined organic layers were dried with dry magnesium sulfate. The volatiles were removed by evaporation and the crude product
was purified chromatographically on silica gel (n-hexane) to give 371 mg (0.820 mmol, 86%) of 3e in form of a light-yellow oil.

R_t (n-hexane) = 0.46. 1H NMR (300 MHz, CDCl3): δ 6.71 (d, 3J_HH = 5.51 Hz, 2H), 7.40 (d, 3J_HH = 5.52 Hz, 2H). 13C NMR (75 MHz, CDCl3): δ 80.4 (C_quat), 130.3 (CH), 131.5 (CH), 137.6 (C_quat). MS (EI) m/z (%): 450 ([M]+, 17), 323 ([M – I]+, 1), 298 (11), 270 (100), 242 (29), 241 ([M – C4HIS]+, 11), 198 (10), 197 (19), 196 ([M – 2 I]+, 55), 153 (10), 128 (17), 116 (19), 115 (61), 114 ([M – C4H2S]6+, 18), 82 ([M – C4H2S2]4+, 5), 71 (14), 69 (12), 45 (10). IR: v [cm⁻¹] = 1485 (m), 1369 (m), 1333 (m), 1150 (m), 868 (s), 804 (m), 702 (s), 648 (m), 615 (m). Anal. calcd. for C₈H₄I₂S₃: C 21.35, H 0.90, S 21.37; Found: C 21.48, H 0.76, S 21.55.

2.5 General procedure 2 (GP2) for the preparation of dithieno[1,4]thiazines 2

In a flame-dried Schlenk vessel under nitrogen atmosphere were charged 1.00 equiv dithienyl sulfide 3, 1.20 equivs aniline (6), 3.00 equivs sodium tert-butoxide, 7.5 mol% bis(dibenzylideneacetone)palladium(0), 15 mol% 1,1′-bis(diphenylphosphino)ferrocene and 6 mL/mmol dry toluene. After degassing with nitrogen for 5 min, the reaction solution was stirred at 100 °C until full conversion of the dithienyl sulfide 3 was observed via TLC. The volatiles were removed by evaporation and the crude product was purified by column chromatography and by recrystallization. For experimental details see table 2.

Table 2. Experimental details GP2.

|   | Aniline (6) [mg] (mmol) | Pd(dba)₂/dppf [mg] (µmol) | NaOBut [mg] (mmol) | t [h] | Dithienothiazine 3 yield [mg] (%) |
|---|------------------------|--------------------------|-------------------|------|---------------------------------|
| 3a | 429 (1.20)             | 135 (1.45)               | 100 (180)         | 346 (3.60) | 19    | 245 (71)                      |
| 3c | 331 (0.930)            | 354 (3.80)               | 78.0 (140)        | 268 (2.79) | 20    | 58.0 (22)                     |
| 3a | 1427 (3.17)            | 354 (3.80)               | 263 (476)         | 914 (9.51) | 18    | 352 (38)                      |
2.5.1 4-Phenyl-4H-dithieno[2,3-b:3',4'-e][1,4]thiazine (2b)

![Chemical Structure]

The crude product was synthesized following GP2 and purified chromatographically on silica gel (n-hexane with 1% triethyl amine) and by recrystallization from n-hexane to give 245 mg (0.850 mmol, 71%) of 2b in form of a beige solid.

Mp.: 116–119 °C. Rf (n-hexane) = 0.35. $^1$H NMR (300 MHz, acetone-d$_6$): $\delta$ 5.66 (d, $^5$J$_{HH}$ = 3.27 Hz, 1H), 6.01 (d, $^5$J$_{HH}$ = 5.50 Hz, 1H), 6.99 (d, $^5$J$_{HH}$ = 3.28 Hz, 1H), 7.14 (d, $^3$J$_{HH}$ = 5.50 Hz, 1H), 7.42 - 7.47 (m, 2H), 7.47 - 7.53 (m, 1H), 7.58 - 7.66 (m, 2H). $^{13}$C NMR (125 MHz, acetone-d$_6$): $\delta$ 101.5 (CH), 117.7 (CH), 117.9 (C$_{quat}$), 119.9 (CH), 123.3 (CH), 129.2 (CH), 129.9 (C$_{quat}$), 130.0 (CH), 131.5 (CH), 142.3 (C$_{quat}$), 143.7 (C$_{quat}$), 144.0 (C$_{quat}$). MS(MALDI-TOF) m/z: 287.678 ([M]+). IR: $\tilde{\nu}$ [cm$^{-1}$] = 3107 (w), 1595 (w), 1553 (m), 1533 (s), 1493 (m), 1439 (m), 1391 (m), 1379 (m), 1366 (m), 1307 (w), 1277 (m), 1265 (m), 1099 (m), 1070 (w), 1051 (w), 1030 (m), 1020 (w), 1001 (w), 880 (w), 856 (m), 829 (w), 799 (m), 760 (s), 738 (s), 685 (s), 644 (m). Anal. calcd. for C$_{14}$H$_9$NS$_3$: C 58.51, H 3.16, N 4.87, S 33.46; Found: C 58.58, H 3.07, N 4.83, S 33.17.

2.5.2 8-Phenyl-8H-dithieno[3,4-b:3',4'-e][1,4]thiazine (2c)

![Chemical Structure]

The crude product was synthesized following GP2 and purified chromatographically on silica gel (n-hexane) and by recrystallization from n-hexane to give 58 mg (0.20 mmol, 22%) of 2c in form of a colorless needles.

Mp.: 136-138 °C. Rf (n-hexane) = 0.31. $^1$H NMR (300 MHz, acetone-d$_6$): $\delta$ 5.60 (d, $^5$J$_{HH}$ = 3.35 Hz, 2H), 7.04 (d, $^5$J$_{HH}$ = 3.32 Hz, 2H), 7.46 - 7.51 (m, 2H), 7.51 - 7.57 (m, 1H), 7.62 - 7.70 (m, 2H). $^{13}$C NMR (75 MHz, acetone-d$_6$): $\delta$ 100.3 (CH), 117.3 (CH), 117.6 (C$_{quat}$), 129.5 (CH), 130.1 (CH), 131.7 (CH), 142.6 (C$_{quat}$), 143.4 (C$_{quat}$). MS(MALDI-TOF) m/z: 286.924
([M]+). IR: $\tilde{\nu} [\text{cm}^{-1}] = 3098$ (w), 2972 (w), 2886 (w), 1595 (w), 1522 (m), 1514 (m), 1489 (m), 1449 (m), 1425 (s), 1379 (m), 1369 (m), 1342 (s), 1273 (m), 1250 (m), 1179 (m), 1161 (m), 1152 (w), 1067 (m), 1038 (m), 1001 (w), 928 (w), 895 (m), 881 (w), 858 m, 835 (w), 822 (m), 748 (s), 698 (s), 691 (m), 677 (m), 622 (m), 610 (s). Anal. calcd. for C$_{14}$H$_9$NS$_3$: C 58.51, H 3.16, N 4.87, S 33.46; Found.: C 58.62, H 3.08, N 4.76, S 33.23.

2.5.3 8-Phenyl-8H-dithieno[3,2-b:2',3'-e][1,4]thiazine (2d)

The crude product was synthesized following GP2 and purified chromatographically on silica gel (n-hexane with 1% triethyl amine) and by recrystallization from ethanol to give 352 mg (1.22 mmol, 38%) of 2d in form of a yellow solid.

Mp.: 97–99 °C. R$_f$ (n-hexane) = 0.35. $^1$H NMR (300 MHz, acetone-d$_6$): $\delta$ 6.59 (d, $^2$$J_{HH} = 5.62$ Hz, 2H), 6.93 (d, $^3$$J_{HH} = 5.62$ Hz, 2H), 7.31 - 7.34 (m, 1H), 7.54 - 7.57 (m, 4H). $^{13}$C NMR (125 MHz, THF-d$_8$): $\delta$ 112.6 (C$_{quat}$), 117.6 (CH), 125.2 (CH), 127.2 (CH), 128.4 (CH), 130.9 (CH), 144.0 (C$_{quat}$), 146.4 (C$_{quat}$). MS(MALDI-TOF) $m/z$: 287.414 ([M]+). IR: $\tilde{\nu} [\text{cm}^{-1}] = 1722$ (w), 1582 (m), 1537 (w), 1512 (w), 1458 (m), 1429 (s), 1358 (w), 1292 (w), 1281 (w), 1252 (m), 1238 (m), 1213 (m), 1180 (m), 1163 (m), 1090 (w), 1067 (m), 1024 (m), 1001 (w), 968 (w), 951 (w), 868 (m), 845 (w), 808 (m), 741 (s), 702 (s), 689 (s), 665 (w), 644 (m), 619 (m). Anal. calcd. for C$_{14}$H$_9$NS$_3$: C 58.51, H 3.16, N 4.87, S 33.46; Found: C 58.44, H 2.99, N 4.80, S 33.07.
3 $^1$H and $^{13}$C NMR spectra

3.1 Bis(4-bromothiophen-3-yl)sulfane (3a)

Figure 1. $^1$H NMR spectrum of 3a (acetone-$d_6$, 293K, 300MHz).

Figure 2. $^{13}$C NMR spectrum of 3a (acetone-$d_6$, 293K, 75MHz).
3.2 Di(thiophen-3-yl)sulfane (3b)

Figure 3. $^1$H NMR spectrum of 3b (CDCl$_3$, 293K, 300MHz).

Figure 4. $^{13}$C NMR spectrum of 3b (CDCl$_3$, 293K, 75MHz).
3.3 Bis(4-bromo thiophen-3-yl)sulfane (3c)

Figure 5. $^1H$ NMR spectrum of 3c (acetone-d$_6$, 293K, 300MHz).

Figure 6. $^{13}C$ NMR spectrum of 3c (acetone-d$_6$, 293K, 75MHz).
3.4 Bis(3-bromo thiophen-2-yl)sulfane (3d)

Figure 7. $^1$H NMR spectrum of 3d (CDCl$_3$, 293K, 300MHz).

Figure 8. $^{13}$C NMR spectrum of 3d (CDCl$_3$, 293K, 75MHz).
3.5 Bis(2-iodothiophen-3-yl)sulfane (3e)

Figure 9. $^1$H NMR spectrum of 3e (CDCl$_3$, 293K, 300MHz).

Figure 10. $^{13}$C NMR spectrum of 3e (CDCl$_3$, 293K, 75MHz).
3.6 4-Phenyl-4H-dithieno[2,3-b:3',4'-e][1,4]thiazine (2b)

Figure 1. $^1$H NMR spectrum of 2b (acetone-d$_6$, 293K, 300MHz).

Figure 12. $^{13}$C NMR spectrum of 2b (acetone-d$_6$, 293K, 75MHz).
3.7 8-Phenyl-8H-dithieno[3,4-b:3',4'-e][1,4]thiazine (2c)

Figure 13. $^1$H NMR spectrum of 2c (acetone-d$_6$, 293K, 300MHz).

Figure 14. $^{13}$C NMR spectrum of 2c (acetone-d$_6$, 293K, 75MHz).
3.8 8-Phenyl-8H-dithieno[3,2-b:2',3'-e][1,4]thiazine (2d)

Figure 15. $^1$H NMR spectrum of 2d (acetone-$d_6$, 293K, 300MHz).

Figure 16. $^{13}$C NMR spectrum of 2d (THF-$d_8$, 293K, 125MHz).
4 Cyclovoltammetric Data

**Figure 17.** Cyclic voltammograms of the dithienothiazines 2b (blue), 2c (red) and 2d (black), (0.1 M [Bu₄N][PF₆], \( \nu = 100 \) mV/s, Pt-working, Ag/AgCl-reference and Pt-counter electrode, [Me₁₀Fc]/[Me₁₀Fc]⁺ as an internal standard; Me₁₀Fc = decamethylferrocene).

**Figure 18.** Measured first oxidation potential \( E_{0/+1}^{exp} \) (0.1 M [Bu₄N][PF₆], \( \nu = 100 \) mV/s, Pt-working, Ag/AgCl-reference and Pt-counter electrode, [Me₁₀Fc]/[Me₁₀Fc]⁺ as an internal standard) vs. HOMO-energies \( E_{HOMO} \) (B3LYP/6-311G*, PCM CH₂Cl₂) of the compounds 1 and 2 in their intra (left) and extra conformation (right).
5 Absorption and Emission Spectra of Compounds 2

Figure 19. Absorption (black, CH$_2$Cl$_2$, T = 298 K, c(2d) = 10$^{-5}$ M) an emission spectrum (red, CH$_2$Cl$_2$, T = 298 K, c(2d) = 10$^{-6}$ M) of 2d.

Figure 20. Absorption (black, CH$_2$Cl$_2$, T = 298 K, c(2a) = 10$^{-5}$ M) an emission spectrum (red, CH$_2$Cl$_2$, T = 298 K, c(2a) = 10$^{-6}$ M) of 2a.
Figure 21. Absorption (black, CH$_2$Cl$_2$, T = 298 K, c(2b) = 10$^{-5}$ M) an emission spectrum (red, CH$_2$Cl$_2$, T = 298 K, c(2b) = 10$^{-6}$ M) of 2b.

Figure 22. Absorption (black, CH$_2$Cl$_2$, T = 298 K, c(2c) = 10$^{-5}$ M) an emission spectrum (red, CH$_2$Cl$_2$, T = 298 K, c(2c) = 10$^{-6}$ M) of 2c.

Figure 23. Absorption (black, CH$_2$Cl$_2$, T = 298 K, c(1) = 10$^{-5}$ M) an emission spectrum (red, CH$_2$Cl$_2$, T = 298 K, c(1) = 10$^{-6}$ M) of 1.
6 Data of Quantum Chemical Calculations

6.1 Computed xyz-coordinates, excitations of compounds 1 and 2 and selected properties derived from the DFT calculations

The ground state geometries of both the intra and the extra conformation of compounds 1 and 2 were optimized using the Gaussian09 program package,[5] the B3LYP functional[6] and the 6-31G* basis set.[7] The ground state geometries of the radical cations were optimized using the Gaussian09 program package,[5] the uB3LYP functional[6] and the 6-311G* basis set.[7] Excitation energies and the excited state geometry (S1) of 2d were calculated with TDDFT[8] methods implemented in the Gaussian09 program package using the same functional and basis set, that were used for the ground state optimizations. All optimized geometries were confirmed as minima by analytical frequency analyses. The polarizable continuum model (PCM) with dichloromethane as a solvent was applied for the calculations each.[9]

For the calculation of redox potentials (see chapter 6.2) the optimized ground state geometries of the intra conformations and the radical cations were reoptimized using the Gaussian09 program package,[5] the uB3LYP functional[6] and the 6-311G* basis set.[7] The reoptimizations were performed in the gas phase and all optimized geometries were confirmed as minima by analytical frequency analyses again. The SMD solvation model with dichloromethane as a solvent was applied afterwards to determine the solvation enthalpies.[10]

Bond orders (Wiberg, Tables 3 and 4) and HOMO compositions (Mulliken, Figure 24) were extracted from the Gaussian09 calculation outputs by the help of the Multiwfn software.[11]

DFT-calculated properties derived from the geometry optimizations of compounds 1 and 2 (S,N-folding angles $\beta$, free enthalpies of switching from extra to intra conformation $\Delta G_{\text{extra\rightarrow\text{intra}}}$ and the HOMO- and LUMO-energies $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$) are listed in table 5.
Table 3. Change of the Wiberg bond-orders from neutral ground-state to the oxidized species (radical cation) $\Delta(D_0-S_0)$ in the dithienothiazine core of compounds 2a, 2c and 2d (uB3LYP/6-311G*).^{[11]}

|     | 1  | 2  | 3  | 4  | 5  | 6  | 7  |
|-----|----|----|----|----|----|----|----|
| 2d  |    |    |    |    |    |    |    |
| $D_0$ | 1.26 & 1.26 & 1.40 & 1.29 & 1.32 & 1.70 & 1.30 |
| $S_0$ | 1.17 & 1.16 & 1.56 & 1.27 & 1.31 & 1.73 & 1.28 |
| $\Delta(D_0-S_0)$ [%] | 7.69 & 8.62 & -10.26 & 1.57 & 0.76 & -1.73 & 1.56 |
| 2a  |    |    |    |    |    |    |    |
| $D_0$ | 1.22 & 1.29 & 1.40 & 1.25 & 1.72 & 1.33 & 1.31 |
| $S_0$ | 1.14 & 1.19 & 1.55 & 1.26 & 1.71 & 1.34 & 1.28 |
| $\Delta(D_0-S_0)$ [%] | 7.02 & 8.40 & -9.68 & -0.79 & 0.58 & -0.75 & 2.34 |
| 2c  |    |    |    |    |    |    |    |
| $D_0$ | 1.24 & 1.25 & 1.16 & 1.48 & 1.43 & 1.34 & 1.64 |
| $S_0$ | 1.16 & 1.19 & 1.20 & 1.61 & 1.31 & 1.34 & 1.66 |
| $\Delta(D_0-S_0)$ [%] | 6.90 & 5.04 & -3.33 & -8.07 & 9.16 & 0.00 & -1.20 |

Table 4. Change of the Wiberg bond-orders from neutral ground-state to the oxidized species (radical cation) $\Delta(D_0-S_0)$ in the phenothiazine core of compound 1 (uB3LYP/6-311G*).^{[11]}

|     | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  |
|-----|----|----|----|----|----|----|----|----|
| 1   |    |    |    |    |    |    |    |    |
| $D_0$ | 1.22 & 1.27 & 1.28 & 1.33 & 1.56 & 1.40 & 1.55 & 1.40 |
| $S_0$ | 1.15 & 1.18 & 1.35 & 1.41 & 1.49 & 1.49 & 1.48 & 1.47 |
| $\Delta(D_0-S_0)$ [%] | 6.09 & 7.63 & -5.19 & -5.67 & 4.70 & -6.04 & 4.73 & -4.76 |

Table 5. DFT-calculated properties derived from the geometry optimizations of compounds 1 and 2: S,N-folding angles of the neutral intra-conformation $\vartheta_{\text{intra}}(S_0)$ and radical cations $\vartheta_{\text{ox}}$, free enthalpies of switching from extra to intra conformation $\Delta G_{\text{extra} \rightarrow \text{intra}}$ and the HOMO- and LUMO-energies of the intra conformations $E_{\text{HOMO,intra}}$ and $E_{\text{LUMO,intra}}$.

|     | $E_{\text{HOMO,intra}}$ | $E_{\text{LUMO,intra}}$ | $\vartheta_{\text{intra}}(S_0)$ | $\vartheta_{\text{ox}}$ | $\Delta G_{\text{extra} \rightarrow \text{intra}}$ |
|-----|-------------------------|-------------------------|-------------------------------|-------------------|-----------------------------|
|     | [eV]                    | [eV]                    | [°]                           | [°]               | [kcal/mol]                  |
| 2d  | -5.012                  | -0.935                  | 144                           | 180               | -1.57                       |
| 2a  | -5.104                  | -1.020                  | 144                           | 180               | -1.01                       |
| 2b  | -5.094                  | -0.878                  | 155                           | 180               | -2.86                       |
| 2c  | -5.310                  | -0.760                  | 158                           | 180               | -4.14                       |
| 1   | -5.357                  | -0.949                  | 148                           | 180               | -1.89                       |

a: B3LYP/6-311G*, PCM CH$_2$Cl$_2$; b: uB3LYP/6-311G*, PCM CH$_2$Cl$_2$
6.1.1.1 Computed xyz coordinates of compound 2a (B3LYP/6-311G* PCM CH₂Cl₂)

**Figure 29.** Optimized ground state geometry of 2a (B3LYP/6-311G* PCM CH₂Cl₂).

| Atom | X (Å)  | Y (Å)  | Z (Å)  |
|------|--------|--------|--------|
| C    | -1.63447 | 1.30254 | 0.19100 |
| C    | -0.27447 | 1.20694 | 0.01879 |
| N    | 0.42941  | -0.00017| 0.22396 |
| C    | -0.27534 | -1.20704| 0.01898 |
| C    | -1.63539 | -1.30156| 0.19115 |
| S    | -2.64737 | 0.00089 | 0.85197 |
| C    | 0.29650  | -2.43894| -0.43755|
| C    | -0.63325 | -3.42170| -0.60521|
| S    | -2.24027 | -2.87481| -0.24590|
| S    | -2.23822 | 2.87595 | -0.24677|
| C    | -0.63098 | 3.42157 | -0.60635|
| C    | 0.29816  | 2.43827 | -0.43831|
| C    | 1.86667  | -0.00054| 0.17205 |
| C    | 2.54046  | -0.00238| -1.05223|
| C    | 3.93389  | -0.00260| -1.07881|
| C    | 4.65636  | -0.00094| 0.11436 |
| C    | 3.98347  | 0.00095 | 1.33532 |
| C    | 2.58959  | 0.00115 | 1.36512 |
| H    | 1.35190  | -2.58106| -0.62534|
| H    | -0.47552 | -4.44065| -0.92567|
| H    | -0.47253 | 4.44033 | -0.92710|
| H    | 1.35365  | 2.57964 | -0.62615|
| H    | 1.97260  | -0.00354| -1.97651|
Computational chemistry

H  4.45408  -0.00404  -2.03081
H  5.74101  -0.00111  0.09182
H  4.54189   0.00226  2.26536
H  2.05366   0.00256  2.30786

SCF Done:  E(RB3LYP) = -1788.38174364  A.U. after  1 cycles
Zero-point correction= 0.190464 (Hartree/Particle)
Thermal correction to Energy= 0.205201
Thermal correction to Enthalpy= 0.206145
Thermal correction to Gibbs Free Energy= 0.146791
Sum of electronic and zero-point Energies= -1788.191280
Sum of electronic and thermal Energies= -1788.176543
Sum of electronic and thermal Enthalpies= -1788.175599
Sum of electronic and thermal Free Energies= -1788.234953

6.1.1.2 Computed excitations of compound 2a (B3LYP/6-311G* PCM CH2Cl2)

Excited State 1:  Singlet-A  3.1379 eV  395.11 nm  f=0.0044  <S**2>=0.000
74 -> 75       0.69268
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1788.26642628
Copying the excited state density for this state as the 1-particle RhoCl density.

Excited State 2:  Singlet-A  3.5682 eV  347.47 nm  f=0.0001  <S**2>=0.000
74 -> 76       0.69625

Excited State 3:  Singlet-A  3.8072 eV  325.66 nm  f=0.0009  <S**2>=0.000
74 -> 75       0.11397
74 -> 78       0.67015
74 -> 79       -0.14571

Excited State 4:  Singlet-A  3.8300 eV  323.72 nm  f=0.0771  <S**2>=0.000
72 -> 75       -0.10163
74 -> 77       0.69486

Excited State 5:  Singlet-A  4.1314 eV  300.10 nm  f=0.0001  <S**2>=0.000

Excited State 6: Singlet-A  4.2713 eV  290.27 nm  f=0.0021  <S**2>=0.000
74 -> 78  0.16351
74 -> 79  0.67781

Excited State 7: Singlet-A  4.7280 eV  262.24 nm  f=0.0101  <S**2>=0.000
73 -> 75  -0.29436
74 -> 81  0.61951

Excited State 8: Singlet-A  4.8178 eV  257.35 nm  f=0.0009  <S**2>=0.000
74 -> 82  0.69322

Excited State 9: Singlet-A  4.8679 eV  254.70 nm  f=0.1784  <S**2>=0.000
73 -> 75  0.62235
74 -> 81  0.28946

Excited State 10: Singlet-A  5.1738 eV  239.64 nm  f=0.0104  <S**2>=0.000
73 -> 76  0.69497

6.1.1.3 Computed xyz coordinates of extra conformation of compound 2a (B3LYP/6-311G* PCM CH2Cl2)

C           1.38451         1.30534         -0.41027
C           0.28958         1.19299         0.40891
N           -0.48834        -0.00001         0.43083
C           0.28962        -1.19299         0.40891
C           1.38454        -1.30533         -0.41027

Figure 30. Optimized ground state geometry of extra conformation of 2a (B3LYP/6-311G* PCM CH2Cl2).
S       1.91495       0.00002      -1.48903
C       0.13539      -2.32338      1.27415
C       1.09480      -3.26926      1.07303
S       2.25632      -2.78562      -0.12848
S       2.25623       2.78568      -0.12849
C       1.09471       3.26929      1.07301
C       0.13533       2.32338      1.27415
C      -1.86249      -0.00002       0.09101
C      -2.56452       1.20530      -0.08597
C      -3.92151       1.19731      -0.39530
C      -4.61775      -0.00004      -0.54642
C      -3.92147      -1.19740      -0.39535
C      -2.56449      -1.20537      -0.08604
H      -0.65751      -2.41855       2.00432
H       1.20094      -4.22992       1.55473
H       1.20081       4.22996       1.55470
H      -0.65753       2.41851       2.00437
H      -2.05200       2.15404       0.00006
H      -4.43334       2.14559      -0.52643
H      -5.67535      -0.00007      -0.78633
H      -4.43330      -2.14567      -0.52653
H     -2.05193      -2.15408       0.00006

SCF Done: E(RB3LYP) = -1788.38113365   A.U. after 1 cycles
Zero-point correction= 0.190644 (Hartree/Particle)
Thermal correction to Energy= 0.205153
Thermal correction to Enthalpy= 0.206098
Thermal correction to Gibbs Free Energy= 0.147799
Sum of electronic and zero-point Energies= -1788.190489
Sum of electronic and thermal Energies= -1788.175980
Sum of electronic and thermal Enthalpies= -1788.175036
Sum of electronic and thermal Free Energies = -1788.233335

### 6.1.1.4 Computed xyz coordinates of radical cation 2a\(^+\) of compound 2a (uB3LYP/6-311G\(^*\) PCM CH\(_2\)Cl\(_2\))

**Figure 31:** Optimized ground state geometry of radical cation of 2a (uB3LYP/6-311G\(^*\) PCM CH\(_2\)Cl\(_2\)).

| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | 1.66255 | 1.30872 | 0.00001 |
| C    | 0.26820  | 1.20627  | -0.00034 |
| N    | -0.40648 | -0.00001 | -0.00033 |
| C    | 0.26821  | -1.20627 | -0.00035 |
| C    | 1.66257  | -1.30871 | 0.00002 |
| S    | 2.79880  | 0.00002  | 0.00051 |
| C    | -0.36174 | -2.48930 | -0.00055 |
| C    | 0.54084  | -3.50421 | -0.00030 |
| S    | 2.19016  | -2.96230 | -0.00002 |
| S    | 2.19012  | 2.96233  | 0.00017 |
| C    | 0.54078  | 3.50421  | -0.00046 |
| C    | -0.36178 | 2.48929  | -0.00055 |
| C    | -1.85940 | -0.00001 | -0.00010 |
| C    | -2.53758 | -0.00012 | 1.21597 |
| C    | -3.93096 | -0.00012 | 1.20963 |
| C    | -4.62559 | -0.00002 | 0.00055 |
| C    | -3.93149 | 0.00009  | -1.20886 |
| C    | -2.53813 | 0.00009  | -1.21586 |
| H    | -1.43141 | -2.63733 | -0.00084 |
| H    | 0.34212  | -4.56553 | -0.00034 |
| H    | 0.34205  | 4.56553  | -0.00061 |
H   -1.43145   2.63731   -0.00087
H   -1.98345   -0.00019   2.14762
H   -4.47070   -0.00021   2.14967
H   -5.70984   -0.00002   0.00075
H   -4.47171   0.00017   -2.14863
H   -1.98443   0.00017   -2.14778

SCF Done: E(UB3LYP) = -1788.21037634 A.U. after 1 cycles
Zero-point correction= 0.191724 (Hartree/Particle)
Thermal correction to Energy= 0.206203
Thermal correction to Enthalpy= 0.207148
Thermal correction to Gibbs Free Energy= 0.148077
Sum of electronic and zero-point Energies= -1788.018652
Sum of electronic and thermal Energies= -1788.004173
Sum of electronic and thermal Enthalpies= -1788.003229
Sum of electronic and thermal Free Energies= -1788.062299

6.1.1.5 Reoptimization of compound 2a (UB3LYP/6-311G*)
Intra conformation of compound 2a in the gas phase (UB3LYP/6-311G*):
SCF Done: E(UB3LYP) = -1788.37535559 A.U. after 1 cycles
Zero-point correction= 0.190566 (Hartree/Particle)
Thermal correction to Energy= 0.205271
Thermal correction to Enthalpy= 0.206215
Thermal correction to Gibbs Free Energy= 0.146948
Sum of electronic and zero-point Energies= -1788.184790
Sum of electronic and thermal Energies= -1788.170085
Sum of electronic and thermal Enthalpies= -1788.169141
Sum of electronic and thermal Free Energies= -1788.228407

Intra conformation of compound 2a in CH₂Cl₂ (UB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -1788.39740489 A.U. after 13 cycles

Extra conformation of compound 2a in the gas phase (UB3LYP/6-311G*):
SCF Done: E(UB3LYP) = -1788.37493912 A.U. after 1 cycles
Zero-point correction= 0.190773 (Hartree/Particle)
Thermal correction to Energy= 0.205259
Thermal correction to Enthalpy= 0.206203
Thermal correction to Gibbs Free Energy= 0.148018
Sum of electronic and zero-point Energies= -1788.184166
Sum of electronic and thermal Energies= -1788.169680
Sum of electronic and thermal Enthalpies= -1788.168736
Sum of electronic and thermal Free Energies= -1788.226921

Extra conformation of compound 2a in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -1788.39632282 A.U. after 13 cycles

Radical cation of compound 2a in the gas phase (uB3LYP/6-311G*):
SCF Done: E(UB3LYP) = -1788.15393212 A.U. after 1 cycles
Zero-point correction= 0.191715 (Hartree/Particle)
Thermal correction to Energy= 0.206191
Thermal correction to Enthalpy= 0.207135
Thermal correction to Gibbs Free Energy= 0.148095
Sum of electronic and zero-point Energies= -1787.962217
Sum of electronic and thermal Energies= -1787.947742
Sum of electronic and thermal Enthalpies= -1787.946797
Sum of electronic and thermal Free Energies= -1788.00583

Radical cation of compound 2a in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -1788.22887656 A.U. after 18 cycles

6.1.2.1 Computed xyz coordinates of compound 2b (B3LYP/6-311G* PCM CH₂Cl₂)

Figure 35. Optimized ground state geometry of 2b (B3LYP/6-311G* PCM CH₂Cl₂).
C  -1.55959  1.52837  0.12714
C   -0.15402  1.21925  0.03834
N    0.34375  -0.08511  0.21155
C   -0.51435  -1.18520  0.01191
C   -1.88071  -1.10105  0.12569
S   -2.77204   0.33327  0.65490
C   -1.83709   2.84290  -0.09646
S   -0.39465   3.76023  -0.38181
C    0.59170   2.33585  -0.23336
C   -0.08483  -2.50570  -0.34561
C   -1.12132  -3.37742  -0.49277
S   -2.65949  -2.61694  -0.23484
C    1.76735  -0.28706  0.15581
C    2.43211  -0.32950  -1.07195
C    3.81136  -0.52552  -1.10706
C    4.52670  -0.67778   0.08081
C    3.86146  -0.63368  1.30526
C    2.48165  -0.43687  1.34415
H   -2.80066   3.32961  -0.07942
H    1.65984   2.40815  -0.35932
H    0.95101  -2.78617  -0.47795
H   -1.08053  -4.42592  -0.74659
H    1.86813  -0.21111  -1.99091
H    4.32610  -0.56092  -2.06135
H    5.60030  -0.83101   0.05143
H    4.41471  -0.75202  2.23080
H    1.95121  -0.39931  2.28924

SCF Done:  E(RB3LYP) = -1788.38694516  A.U. after  1 cycles
Zero-point correction= 0.190446 (Hartree/Particle)
Thermal correction to Energy= 0.205151
Thermal correction to Enthalpy= 0.206096
Thermal correction to Gibbs Free Energy= 0.146731
Sum of electronic and zero-point Energies= -1788.196499
Sum of electronic and thermal Energies= -1788.181794
Sum of electronic and thermal Enthalpies= -1788.180850
Sum of electronic and thermal Free Energies= -1788.240214

6.1.2.2 Computed excitations of compound 2b (B3LYP/6-311G* PCM CH₂Cl₂)

Excited State  1:  Singlet-A  3.5193 eV  352.30 nm  f=0.0225  <S**2>=0.000
  74 -> 75  0.64543
  74 -> 76  0.26081
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1788.25761242
Copying the excited state density for this state as the 1-particle RhoCl density.

Excited State  2:  Singlet-A  3.6485 eV  339.82 nm  f=0.0094  <S**2>=0.000
  74 -> 75  -0.22516
  74 -> 76  0.56576
  74 -> 77  -0.33974

Excited State  3:  Singlet-A  3.8036 eV  325.96 nm  f=0.0893  <S**2>=0.000
  74 -> 75  -0.11194
  74 -> 76  0.31663
  74 -> 77  0.61297

Excited State  4:  Singlet-A  3.9500 eV  313.88 nm  f=0.0304  <S**2>=0.000
  74 -> 78  0.65400
  74 -> 79  -0.21752

Excited State  5:  Singlet-A  4.2506 eV  291.68 nm  f=0.0211  <S**2>=0.000
  74 -> 78  0.22920
  74 -> 79  0.65209

Excited State  6:  Singlet-A  4.5083 eV  275.01 nm  f=0.0044  <S**2>=0.000
  74 -> 80  0.69176

Excited State  7:  Singlet-A  4.6127 eV  268.79 nm  f=0.0167  <S**2>=0.000
Excited State 8: Singlet-A 4.7044 eV 263.55 nm \( f=0.1263 \) \( <S^2>=0.000 \)
- 73 -> 75: -0.26544
- 74 -> 81: 0.62400

Excited State 9: Singlet-A 4.8099 eV 257.77 nm \( f=0.0301 \) \( <S^2>=0.000 \)
- 73 -> 75: -0.10351
- 73 -> 76: 0.61610
- 73 -> 77: -0.28735

Excited State 10: Singlet-A 4.9775 eV 249.09 nm \( f=0.0332 \) \( <S^2>=0.000 \)
- 73 -> 76: 0.25422
- 73 -> 77: 0.61329
- 73 -> 78: -0.21146

6.1.2.3 Computed xyz coordinates of extra conformation of compound 2b (B3LYP/6-311G* PCM CH₂Cl₂)

![Figure 36. Optimized ground state geometry of extra conformation of 2b (B3LYP/6-311G* PCM CH₂Cl₂).](image)

|   |   |   |
|---|---|---|
| C | -1.41050 | 1.35955 | 0.53658 |
| C | -0.27218 | 1.21109 | -0.33050 |
| N | 0.42983  | -0.02382 | -0.40908 |
| C | -0.42098 | -1.16484 | -0.43803 |
| C | -1.50473 | -1.26053 | 0.39771  |
| S | -1.94624 | -0.00129 | 1.56201  |
|   |   |   |   |
|---|---|---|---|
| C | -1.98605 | 2.59224 | 0.46999 |
| S | -1.13886 | 3.61455 | -0.64654 |
| C | -0.03331 | 2.34542 | -1.05609 |
| C | -0.34332 | -2.25242 | -1.36601 |
| C | -1.34994 | -3.15396 | -1.19724 |
| S | -2.46236 | -2.67209 | 0.05122 |
| C | 1.80551 | -0.14639 | -0.08862 |
| C | 2.64163 | 0.97820 | 0.01948 |
| C | 3.99161 | 0.83227 | 0.32598 |
| C | 4.55253 | -0.42657 | 0.52961 |
| C | 3.72597 | -1.54413 | 0.43700 |
| C | 2.37269 | -1.41306 | 0.13969 |
| H | -2.84805 | 2.96328 | 1.00306 |
| H | 0.72405 | 2.51286 | -1.80598 |
| H | 0.43642 | -2.35264 | -2.10982 |
| H | -1.51675 | -4.08048 | -1.72615 |
| H | 2.24141 | 1.97258 | -0.11894 |
| H | 4.60774 | 1.72253 | 0.40514 |
| H | 5.60661 | -0.53351 | 0.76114 |
| H | 4.12997 | -2.53708 | 0.60794 |
| H | 1.75553 | -2.30078 | 0.10282 |

SCF Done: E(RB3LYP) = -1788.38342091 A.U. after 1 cycles
Zero-point correction= 0.190634 (Hartree/Particle)
Thermal correction to Energy= 0.205098
Thermal correction to Enthalpy= 0.206042
Thermal correction to Gibbs Free Energy= 0.147764
Sum of electronic and zero-point Energies= -1788.192787
Sum of electronic and thermal Energies= -1788.178323
Sum of electronic and thermal Enthalpies= -1788.177379
Sum of electronic and thermal Free Energies= -1788.235657
6.1.2.4 Computed xyz coordinates of radical cation 2b* of compound 2b (uB3LYP/6-311G* PCM CH₂Cl₂)

Figure 37. Optimized ground state geometry of radical cation of 2b (uB3LYP/6-311G* PCM CH₂Cl₂).

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| C    | 1.52093 | 1.58371 | -0.00005 |
| C    | 0.12322 | 1.22004 | 0.00005 |
| N    | -0.32563 | -0.09757 | 0.00008 |
| C    | 0.53521 | -1.16301 | 0.00002 |
| C    | 1.93810 | -1.03132 | -0.00003 |
| S    | 2.84505 | 0.43287 | 0.00022 |
| C    | 1.71495 | 2.93745 | -0.00115 |
| S    | 0.21652 | 3.78043 | -0.00113 |
| C    | -0.69408 | 2.32841 | -0.0003 |
| C    | 0.12807 | -2.53546 | 0.0001 |
| C    | 1.18443 | -3.38513 | -0.0001 |
| S    | 2.72738 | -2.57907 | -0.0007 |
| C    | -1.75836 | -0.34021 | 0.00006 |
| C    | -2.42731 | -0.45110 | 1.21614 |
| C    | -3.80111 | -0.68349 | 1.20924 |
| C    | -4.48563 | -0.79971 | -0.0003 |
| C    | -3.80098 | -0.68383 | -1.20925 |
| C    | -2.42717 | -0.45145 | -1.21605 |
| H    | 2.64907 | 3.47781 | -0.00024 |
| H    | -1.77126 | 2.35888 | 0.0002 |
| H    | -0.90237 | -2.85823 | 0.0006 |
| H    | 1.16371 | -4.46476 | -0.0004 |
H  -1.88178  -0.35859  2.14828
H  -4.33343  -0.77393  2.14916
H  -5.55452  -0.98156  -0.00005
H  -4.33317  -0.77453  -2.14923
H  -1.88155  -0.35919  -2.14816

SCF Done:  \( E(\text{UB3LYP}) = -1788.2081216 \) A.U. after 1 cycles
Zero-point correction= 0.191468 (Hartree/Particle)
Thermal correction to Energy= 0.205931
Thermal correction to Enthalpy= 0.206875
Thermal correction to Gibbs Free Energy= 0.147770
Sum of electronic and zero-point Energies= -1788.016653
Sum of electronic and thermal Energies= -1788.002190
Sum of electronic and thermal Enthalpies= -1788.001246
Sum of electronic and thermal Free Energies= -1788.060351

6.1.2.5 Reoptimization of compound 2b (uB3LYP/6-311G*)
Intra conformation of compound 2b in the gas phase (uB3LYP/6-311G*):
SCF Done:  \( E(\text{UB3LYP}) = -1788.38068827 \) A.U. after 1 cycles
Zero-point correction= 0.190572 (Hartree/Particle)
Thermal correction to Energy= 0.205257
Thermal correction to Enthalpy= 0.206201
Thermal correction to Gibbs Free Energy= 0.146833
Sum of electronic and zero-point Energies= -1788.190116
Sum of electronic and thermal Energies= -1788.175431
Sum of electronic and thermal Enthalpies= -1788.174487
Sum of electronic and thermal Free Energies= -1788.233855

Intra conformation of compound 2b in CH\(_2\)Cl\(_2\) (uB3LYP/6-311G* SMD CH\(_2\)Cl\(_2\)):
SCF Done:  \( E(\text{UB3LYP}) = -1788.40238287 \) A.U. after 13 cycles

Extra conformation of compound 2b in the gas phase (uB3LYP/6-311G*):
SCF Done:  \( E(\text{UB3LYP}) = -1788.37703184 \) A.U. after 1 cycles
Zero-point correction= 0.190735 (Hartree/Particle)
Thermal correction to Energy= 0.205188
Thermal correction to Enthalpy= 0.206132
Thermal correction to Gibbs Free Energy= 0.147890
Sum of electronic and zero-point Energies= -1788.186297
Sum of electronic and thermal Energies= -1788.171844
Sum of electronic and thermal Enthalpies= -1788.170900
Sum of electronic and thermal Free Energies= -1788.229142

Extra conformation of compound 2b in CH$_2$Cl$_2$ (uB3LYP/6-311G* SMD CH$_2$Cl$_2$):
SCF Done:  E(UB3LYP) = -1788.39877208     A.U. after  13 cycles

Radical cation of compound 2b in the gas phase (uB3LYP/6-311G*):
SCF Done:  E(UB3LYP) = -1788.15163876     A.U. after  1 cycles
Zero-point correction= 0.191341 (Hartree/Particle)
Thermal correction to Energy= 0.205854
Thermal correction to Enthalpy= 0.206798
Thermal correction to Gibbs Free Energy= 0.147335
Sum of electronic and zero-point Energies= -1787.960298
Sum of electronic and thermal Energies= -1787.945785
Sum of electronic and thermal Enthalpies= -1787.944840
Sum of electronic and thermal Free Energies= -1788.004303

Radical cation of compound 2b in CH$_2$Cl$_2$ (uB3LYP/6-311G* SMD CH$_2$Cl$_2$):
SCF Done:  E(UB3LYP) = -1788.22691472     A.U. after  19 cycles

6.1.3.1 Computed xyz coordinates of compound 2c (B3LYP/6-311G* PCM CH$_2$Cl$_2$)

Figure 32. Optimized ground state geometry of 2c (B3LYP/6-311G* PCM CH$_2$Cl$_2$).
|  | X    | Y    | Z    |
|---|------|------|------|
| C | -1.82222 | -1.34089 | 0.11313 |
| C | -0.39025 | -1.22099 | 0.01252 |
| N | 0.28127 | -0.00038 | 0.19775 |
| C | -0.38820 | 1.22136 | 0.01257 |
| C | -1.81993 | 1.34381 | 0.11334 |
| S | -2.86642 | 0.00231 | 0.62245 |
| C | -2.27108 | -2.60988 | -0.10261 |
| S | -0.96484 | -3.70772 | -0.39782 |
| C | 0.20079 | -2.42625 | -0.26534 |
| C | 0.20496 | 2.42552 | -0.26564 |
| S | -0.95847 | 3.70909 | -0.39798 |
| C | -2.26656 | 2.61359 | -0.10235 |
| C | 1.71989 | -0.00148 | 0.15499 |
| C | 2.43664 | -0.00175 | 1.35113 |
| C | 3.83039 | -0.00259 | 1.32427 |
| C | 4.50600 | -0.00325 | 0.10447 |
| C | 3.78716 | -0.00292 | -1.09080 |
| C | 2.39354 | -0.00194 | -1.06815 |
| H | -3.29011 | -2.96565 | -0.08099 |
| H | 1.24910 | -2.63928 | -0.39809 |
| H | 1.25364 | 2.63655 | -0.39865 |
| H | -3.28495 | 2.97121 | -0.08077 |
| H | 1.89818 | -0.00129 | 2.29242 |
| H | 4.38683 | -0.00281 | 2.25543 |
| H | 5.59070 | -0.00398 | 0.08488 |
| H | 4.31014 | -0.00335 | -2.04124 |
| H | 1.82663 | -0.00153 | -1.99277 |

SCF Done: E(RB3LYP) = -1788.39151388 A.U. after 1 cycles
Zero-point correction= 0.190442 (Hartree/Particle)
Thermal correction to Energy= 0.205062
Thermal correction to Enthalpy = 0.206006
Thermal correction to Gibbs Free Energy = 0.147163
Sum of electronic and zero-point Energies = -1788.201071
Sum of electronic and thermal Energies = -1788.186452
Sum of electronic and thermal Enthalpies = -1788.185507
Sum of electronic and thermal Free Energies = -1788.244351

6.1.3.2 Computed excitations of compound 2c (B3LYP/6-311G* PCM CH₂Cl₂)

Excited State 1: Singlet-A
Energy = 3.7819 eV, λ = 327.83 nm, f = 0.0125, <S²> = 0.000
74 -> 75: 0.59834
74 -> 76: 0.35385
This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1788.25253071
Copying the excited state density for this state as the 1-particle RhoCl density.

Excited State 2: Singlet-A
Energy = 3.9191 eV, λ = 316.36 nm, f = 0.0537, <S²> = 0.000
74 -> 75: -0.34309
74 -> 76: 0.59773
74 -> 78: -0.12096

Excited State 3: Singlet-A
Energy = 4.1292 eV, λ = 300.26 nm, f = 0.0173, <S²> = 0.000
74 -> 77: 0.69936

Excited State 4: Singlet-A
Energy = 4.2243 eV, λ = 293.50 nm, f = 0.2299, <S²> = 0.000
74 -> 75: -0.10707
74 -> 78: 0.67010
74 -> 80: -0.13592

Excited State 5: Singlet-A
Energy = 4.5274 eV, λ = 273.85 nm, f = 0.0221, <S²> = 0.000
73 -> 75: 0.21647
73 -> 80: 0.21752
74 -> 78: 0.13686
74 -> 80: 0.61395

Excited State 6: Singlet-A
Energy = 4.5688 eV, λ = 271.37 nm, f = 0.0003, <S²> = 0.000
74 -> 79: 0.70038
Excited State 7: Singlet-A 4.6114 eV 268.86 nm f=0.0163 <S**2>=0.000
73 -> 75 0.60682
73 -> 76 0.27473
74 -> 80 -0.19628

Excited State 8: Singlet-A 4.6973 eV 263.95 nm f=0.0194 <S**2>=0.000
73 -> 75 -0.24911
73 -> 76 0.64031

Excited State 9: Singlet-A 4.7742 eV 259.69 nm f=0.0085 <S**2>=0.000
73 -> 77 0.69637

Excited State 10: Singlet-A 4.9228 eV 251.86 nm f=0.0238 <S**2>=0.000
73 -> 78 0.67888
73 -> 80 -0.10233

6.1.3.3 Computed xyz coordinates of extra conformation of compound 2c (B3LYP/6-311G* PCM CH₂Cl₂)

Figure 33. Optimized ground state geometry of extra conformation of 2c (B3LYP/6-311G* PCM CH₂Cl₂).

C 1.51291 1.32019 0.54804
C 0.40986 1.18780 -0.36634
N -0.37109 -0.00002 -0.40615
C 0.40992 -1.18778 -0.36634
C 1.51299 -1.32005 0.54804
S 1.92141 0.00008 1.67377
C 2.16200 2.51287 0.43712
S 1.42933 3.51337 -0.77721
C 0.27218 2.28612 -1.16832
|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| C | 0.27239   | -2.28613  | -1.16832  |
| S | 1.42967   | -3.51325  | -0.77719  |
| C | 2.16223   | -2.51264  | 0.43714   |
| C | -1.75806  | -0.00005  | -0.09643  |
| C | -2.46522  | -1.20396  | 0.06754   |
| C | -3.82403  | -1.19631  | 0.36941   |
| C | -4.52204  | -0.00019  | 0.51878   |
| C | -3.82416  | 1.19596   | 0.36946   |
| C | -2.46532  | 1.20377   | 0.06758   |
| H | 3.02126   | 2.86551   | 0.98689   |
| H | -0.44983  | 2.45255   | -1.95296  |
| H | -0.44967  | -2.45270  | -1.95289  |
| H | 3.02156   | -2.86517  | 0.98686   |
| H | -1.95539  | -2.15267  | -0.02485  |
| H | -4.33648  | -2.14558  | 0.49105   |
| H | -5.58191  | -0.00027  | 0.74856   |
| H | -4.33665  | 2.14521   | 0.49113   |
| H | -1.95563  | 2.15255   | -0.02482  |

SCF Done: \( E(\text{RB3LYP}) = -1788.38543013 \) A.U. after 1 cycles

Zero-point correction= 0.190631 (Hartree/Particle)
Thermal correction to Energy= 0.205051
Thermal correction to Enthalpy= 0.205996
Thermal correction to Gibbs Free Energy= 0.147678

Sum of electronic and zero-point Energies= -1788.194799
Sum of electronic and thermal Energies= -1788.180379
Sum of electronic and thermal Enthalpies= -1788.179435
Sum of electronic and thermal Free Energies= -1788.237752
6.1.3.4 Computed xyz coordinates of radical cation 2c+ of compound 2c (uB3LYP/6-311G* PCM CH2Cl2)

Figure 34. Optimized ground state geometry of radical cation of 2c (uB3LYP/6-311G* PCM CH2Cl2).

| Element | X       | Y       | Z       | Error  |
|---------|---------|---------|---------|--------|
| C       | -1.84393| -1.34236| 0.00001 |
| C       | -0.40014| -1.21048| 0.00001 |
| N       | 0.26029 | 0.00000 | 0.00001 |
| C       | -0.40013| 1.21048  | 0.00001 |
| C       | -1.84393| 1.34237  | 0.00001 |
| S       | -2.96813| 0.00000  | 0.00030 |
| C       | -2.24184| -2.64913 | -0.00013|
| S       | -0.89155| -3.72214 | -0.00015|
| C       | 0.23352 | -2.44352 | 0.00000 |
| C       | 0.23353 | 2.44352  | -0.00000|
| S       | -0.89154| 3.72214  | -0.00015|
| C       | -2.24184| 2.64914  | -0.00013|
| C       | 1.71470 | 0.00000  | 0.00002 |
| C       | 2.39077 | 0.00001  | 1.21708 |
| C       | 3.78399 | 0.00001  | 1.20954 |
| C       | 4.47796 | 0.00001  | 0.00006 |
| C       | 3.78401 | 0.00001  | -1.20944|
| C       | 2.39081 | 0.00001  | -1.21704|
| H       | -3.24754| -3.04022 | -0.00024|
| H       | 1.29231 | -2.64366 | 0.00007 |
| H       | 1.29231 | 2.64366  | 0.00006 |
| H       | -3.24754| 3.04023  | -0.00024|
H  1.83637  0.00001  2.14841
H  4.32398  0.00001  2.14935
H  5.56217  -0.00001  0.00007
H  4.32403  -0.00002 -2.14924
H  1.83645  -0.00002 -2.14839

SCF Done:  E(UB3LYP) = -1788.20232791 A.U. after 1 cycles
Zero-point correction= 0.191003 (Hartree/Particle)
Thermal correction to Energy= 0.205500
Thermal correction to Enthalpy= 0.206444
Thermal correction to Gibbs Free Energy= 0.147283
Sum of electronic and zero-point Energies= -1788.011325
Sum of electronic and thermal Energies= -1787.996828
Sum of electronic and thermal Enthalpies= -1787.995884
Sum of electronic and thermal Free Energies= -1788.055045

6.1.3.5 Reoptimization of compound 2c (UB3LYP/6-311G*)

Intra conformation of compound 2c in the gas phase (UB3LYP/6-311G*):
SCF Done:  E(UB3LYP) = -1788.38535920 A.U. after 1 cycles
Zero-point correction= 0.190610 (Hartree/Particle)
Thermal correction to Energy= 0.205200
Thermal correction to Enthalpy= 0.206144
Thermal correction to Gibbs Free Energy= 0.147407
Sum of electronic and zero-point Energies= -1788.194750
Sum of electronic and thermal Energies= -1788.180159
Sum of electronic and thermal Enthalpies= -1788.179215
Sum of electronic and thermal Free Energies= -1788.237952

Intra conformation of compound 2c in CH$_2$Cl$_2$ (UB3LYP/6-311G* SMD CH$_2$Cl$_2$):
SCF Done:  E(UB3LYP) = -1788.40687300 A.U. after 13 cycles

Extra conformation of compound 2c in the gas phase (UB3LYP/6-311G*):
SCF Done:  E(UB3LYP) = -1788.37887704 A.U. after 1 cycles
Zero-point correction = 0.190740 (Hartree/Particle)
Thermal correction to Energy = 0.205148
Thermal correction to Enthalpy = 0.206092
Thermal correction to Gibbs Free Energy = 0.147855
Sum of electronic and zero-point Energies = -1788.188137
Sum of electronic and thermal Energies = -1788.173729
Sum of electronic and thermal Enthalpies = -1788.172785
Sum of electronic and thermal Free Energies = -1788.231022

Extra conformation of compound 2c in CH2Cl2 (uB3LYP/6-311G* SMD CH2Cl2):
SCF Done: E(UB3LYP) = -1788.40070394 A.U. after 13 cycles

Radical cation of compound 2c in the gas phase (uB3LYP/6-311G*):
SCF Done: E(UB3LYP) = -1788.14600330 A.U. after 1 cycles
Zero-point correction = 0.190951 (Hartree/Particle)
Thermal correction to Energy = 0.205458
Thermal correction to Enthalpy = 0.206402
Thermal correction to Gibbs Free Energy = 0.147069
Sum of electronic and zero-point Energies = -1787.955052
Sum of electronic and thermal Energies = -1787.940546
Sum of electronic and thermal Enthalpies = -1787.939602
Sum of electronic and thermal Free Energies = -1787.998934

Radical cation of compound 2c in CH2Cl2 (uB3LYP/6-311G* SMD CH2Cl2):
SCF Done: E(UB3LYP) = -1788.22166994 A.U. after 18 cycles

6.1.4.1 Computed xyz coordinates of compound 2d (B3LYP/6-311G* PCM CH2Cl2)

\[ \text{Figure 25. Optimized ground state geometry of 2d (B3LYP/6-311G* PCM CH2Cl2).} \]
C  -1.90116  -1.33370  0.22578
C  -0.55493  -1.19071  0.01390
N   0.16467   -0.00011  0.16614
C  -0.55436   1.19080  0.01364
C  -1.90052  1.33455  0.22545
S  -2.88058   0.00075  0.90939
S    0.14399   2.66274  -0.63408
C  -1.40452  3.46260  -0.56204
C  -2.38720  2.63274  -0.11475
C  -2.38853  2.63172  -0.11407
C  -1.40631  -3.46222  -0.56116
S    0.14263  -2.66316  -0.63342
C   1.60230   -0.00034  0.21779
C   2.24356   0.00097  1.45743
C   3.63509   0.00082  1.51425
C   4.38337  -0.00067  0.33674
C   3.74056  -0.00197  -0.89994
C   2.34765  -0.00177  -0.96342
H   -1.47175  4.50594  -0.83097
H   -3.42071  2.93456   0.00114
H   -3.42218  -2.93299   0.00202
H   -1.47407  -4.50559  -0.82984
H    1.64801   0.00207  2.36347
H    4.13450   0.00185  2.47707
H    5.46714  -0.00081  0.38378
H    4.32060  -0.00311 -1.81637
H    1.83909  -0.00267 -1.92114

SCF Done: E(RB3LYP) = -1788.38186266 A.U. after 1 cycles
Zero-point correction= 0.189972 (Hartree/Particle)
Thermal correction to Energy= 0.204881
Thermal correction to Enthalpy = 0.205825
Thermal correction to Gibbs Free Energy = 0.145244
Sum of electronic and zero-point Energies = -1788.191890
Sum of electronic and thermal Energies = -1788.176982
Sum of electronic and thermal Enthalpies = -1788.176038
Sum of electronic and thermal Free Energies = -1788.236619

6.1.4.2 Computed excitations of compound 2d (B3LYP/6-311G* PCM CH2Cl2)
Excited State 1: Singlet-A  3.2372 eV  383.00 nm  f=0.0609  <S**2>=0.000
                   74 -> 75  0.69419
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1788.26289842
Copying the excited state density for this state as the 1-particle RhoCl density.

Excited State 2: Singlet-A  3.4536 eV  359.00 nm  f=0.0023  <S**2>=0.000
                   74 -> 76  0.69883

Excited State 3: Singlet-A  3.6051 eV  343.91 nm  f=0.0000  <S**2>=0.000
                   74 -> 77  0.70054

Excited State 4: Singlet-A  3.9338 eV  315.18 nm  f=0.0290  <S**2>=0.000
                   74 -> 78  0.67032
                   74 -> 80  0.19148

Excited State 5: Singlet-A  4.1466 eV  299.00 nm  f=0.0178  <S**2>=0.000
                   74 -> 79  0.69351

Excited State 6: Singlet-A  4.3283 eV  286.45 nm  f=0.0109  <S**2>=0.000
                   74 -> 78  -0.18241
                   74 -> 80  0.67023

Excited State 7: Singlet-A  4.9021 eV  252.92 nm  f=0.1317  <S**2>=0.000
                   73 -> 75  0.66069
                   74 -> 81  -0.16604
                   74 -> 84  0.10517

Excited State 8: Singlet-A  5.0217 eV  246.90 nm  f=0.0383  <S**2>=0.000
72 -> 80  -0.11191
73 -> 75  0.12728
73 -> 76  0.17442
73 -> 77  0.11542
73 -> 79  -0.13802
74 -> 81  0.62464

Excited State 9: Singlet-A 5.0790 eV 244.11 nm f=0.0127 <S**2>=0.000
73 -> 76  0.67619
74 -> 81  -0.16458

Excited State 10: Singlet-A 5.1928 eV 238.76 nm f=0.0270 <S**2>=0.000
73 -> 75  -0.11010
73 -> 77  0.68145
74 -> 81  -0.11468

6.1.4.3 Computed xyz coordinates of $S_1$ of compound 2d (B3LYP/6-311G* PCM CH$_2$Cl$_2$)

|     |     |     |     |
|-----|-----|-----|-----|
| C   | 1.95631 | 1.32829 | -0.15993 |
| C   | 0.53983 | 1.19471 | -0.16805 |
| N   | -0.13176 | -0.00293 | -0.04547 |
| C   | 0.54906 | -1.19066 | 0.01480 |
| C   | 1.96504 | -1.32735 | 0.02752 |
| S   | 3.03600 | 0.00844 | 0.26029 |
| S   | -0.23889 | -2.76455 | -0.18906 |
| C   | 1.34121 | -3.55336 | -0.21828 |
| C   | 2.37859 | -2.67920 | -0.09049 |
| C   | 2.36027 | 2.68884 | -0.08852 |
| C   | 1.32210 | 3.56285 | 0.03042 |

Figure 26. Optimized $S_1$ geometry of 2d (B3LYP/6-311G* PCM CH$_2$Cl$_2$).
|  | x         | y         | z         |
|---|-----------|-----------|-----------|
| S | -0.26163  | 2.78058   | 0.09801   |
| C | -1.57412  | -0.00606  | 0.00331   |
| C | -2.22181  | -0.42494  | 1.16557   |
| C | -3.61410  | -0.43007  | 1.20277   |
| C | -4.34724  | -0.01969  | 0.08994   |
| C | -3.68866  | 0.39745   | -1.06682  |
| C | -2.29725  | 0.40468   | -1.11668  |
| H | 1.38207   | -4.62493  | -0.34312  |
| H | 3.41763   | -2.98564  | -0.08923  |
| H | 3.39717   | 3.00360   | -0.10638  |
| H | 1.36611   | 4.64048   | 0.08709   |
| H | -1.63977  | -0.73092  | 2.02698   |
| H | -4.12397  | -0.74973  | 2.10479   |
| H | -5.43124  | -0.02527  | 0.12363   |
| H | -4.25697  | 0.71217   | -1.93501  |
| H | -1.77174  | 0.71631   | -2.01168  |

Excited State 1: Singlet-?Sym 2.1926 eV 565.47 nm f=0.0597 $<S^2>=0.000$

This state for optimization and/or second-order correction.

Total Energy, $E(TD-HF/TD-KS) = -1788.28415837$

SCF Done: $E(RB3LYP) = -1788.36473410$ A.U. after 7 cycles

Zero-point correction= 0.187239 (Hartree/Particle)

Thermal correction to Energy= 0.202844

Thermal correction to Enthalpy= 0.203788

Thermal correction to Gibbs Free Energy= 0.142779

Sum of electronic and zero-point Energies= -1788.096920

Sum of electronic and thermal Energies= -1788.081315

Sum of electronic and thermal Enthalpies= -1788.080371

Sum of electronic and thermal Free Energies= -1788.141380
6.1.4.4 Computed excitations of $S_1$ (emission of $S_1$) of compound 2d (B3LYP/6-311G* PCM CH$_2$Cl$_2$)

Excited State 1: Singlet-A 2.2118 eV  560.55 nm  f=0.0436  <S**2>=0.000

74 -> 75  0.70329

This state for optimization and/or second-order correction.

Total Energy, $E$(TD-HF/TD-KS) = -1788.28345089

Copying the excited state density for this state as the 1-particle RhoCl density.

6.1.4.5 Computed xyz coordinates of extra conformation of compound 2d (B3LYP/6-311G* PCM CH$_2$Cl$_2$)

![Figure 27. Optimized ground state geometry of extra conformation of 2d (B3LYP/6-311G* PCM CH$_2$Cl$_2$).](image)

C  1.47465  1.42957  0.55167
C  0.44201  1.16428 -0.30572
N -0.26676 -0.05381 -0.36010
C  0.57757 -1.17569 -0.19247
C  1.63149 -1.21857  0.68232
S  2.01832  0.18789  1.71420
S  0.58485 -2.59169 -1.23302
C  1.95088 -3.24913 -0.38605
C  2.41221 -2.40910  0.58265
C  2.08392  2.70316  0.33491
C  1.50556  3.38013 -0.69663
S  0.23693  2.46965 -1.46162
C -1.65173 -0.09464  0.00072
C -2.27332  1.03097  0.55897
C  -3.62741  1.00087  0.88200  
C  -4.38698 -0.14688  0.66623  
C  -3.76822 -1.26963  0.12033  
C  -2.41742 -1.24814 -0.21621  
H   2.31959 -4.22864 -0.65279  
H   3.26966 -2.62311  1.20761  
H   2.90686  3.08894  0.92263  
H   1.74087  4.36950 -1.06044  
H  -1.69748  1.92572  0.75742  
H  -4.08421  1.88375  1.31753  
H  -5.44111 -0.16692  0.92043  
H  -4.33911 -2.17560 -0.05575  
H  -1.96868 -2.13386 -0.64531  

SCF Done:  E(RB3LYP) = -1788.38140110  A.U. after 1 cycles
Zero-point correction= 0.190430 (Hartree/Particle)
Thermal correction to Energy= 0.204998
Thermal correction to Enthalpy= 0.205943
Thermal correction to Gibbs Free Energy= 0.147288
Sum of electronic and zero-point Energies= -1788.190971
Sum of electronic and thermal Energies= -1788.176403
Sum of electronic and thermal Enthalpies= -1788.175458
Sum of electronic and thermal Free Energies= -1788.234114

6.1.4.6 Computed excitations of extra conformation of compound 2d (B3LYP/6-311G*  
PCM CH₂Cl₂)
Excited State 1:    Singlet-A    3.8539 eV  321.71 nm  f=0.0327  <S**2>=0.000  
74 ->  75   0.37034  
74 ->  76   0.59063  
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1788.23977339
Copying the excited state density for this state as the 1-particle RhoCl density.
| Excited State | Singlet-A  | Energy (eV) | Wavelength (nm) | f | <S^2> |
|--------------|------------|-------------|----------------|---|--------|
| 2            | 3.8866     | 319.01      | 0.0691         | 0.000 |        |
| 74 -> 75     | 0.58877    |             |                |     |        |
| 74 -> 76     | -0.36995   |             |                |     |        |
| 3            | 4.4049     | 281.47      | 0.0089         | 0.000 |        |
| 73 -> 76     | 0.10036    |             |                |     |        |
| 74 -> 77     | 0.65314    |             |                |     |        |
| 74 -> 78     | 0.10490    |             |                |     |        |
| 74 -> 79     | -0.16946   |             |                |     |        |
| 4            | 4.6266     | 267.98      | 0.0835         | 0.000 |        |
| 73 -> 76     | 0.11720    |             |                |     |        |
| 74 -> 77     | -0.20487   |             |                |     |        |
| 74 -> 78     | 0.50221    |             |                |     |        |
| 74 -> 79     | -0.37785   |             |                |     |        |
| 74 -> 80     | 0.14738    |             |                |     |        |
| 5            | 4.6396     | 267.23      | 0.0389         | 0.000 |        |
| 73 -> 75     | -0.31344   |             |                |     |        |
| 73 -> 76     | -0.12247   |             |                |     |        |
| 74 -> 78     | 0.35554    |             |                |     |        |
| 74 -> 79     | 0.46292    |             |                |     |        |
| 74 -> 80     | 0.15870    |             |                |     |        |
| 6            | 4.7587     | 260.54      | 0.0712         | 0.000 |        |
| 72 -> 76     | -0.11597   |             |                |     |        |
| 73 -> 75     | 0.59178    |             |                |     |        |
| 74 -> 78     | 0.24413    |             |                |     |        |
| 74 -> 79     | 0.20730    |             |                |     |        |
| 7            | 4.8419     | 256.06      | 0.0630         | 0.000 |        |
| 73 -> 76 | 0.65579 |
| 74 -> 79 | 0.19874 |

**Excited State 8:** Singlet-A

| 73 -> 75 | 0.13628 |
| 74 -> 78 | -0.17689 |
| 74 -> 80 | 0.63864 |

| 73 -> 75 | 0.68116 |
| 74 -> 78 | 0.17689 |
| 74 -> 80 | 0.63864 |

**Excited State 9:** Singlet-A

| 72 -> 75 | 0.68116 |

**Excited State 10:** Singlet-A

| 71 -> 75 | -0.18872 |
| 71 -> 78 | -0.11184 |
| 72 -> 76 | -0.22884 |
| 73 -> 77 | 0.57445 |

### 6.1.4.7 Computed xyz coordinates of radical cation 2d⁺ of compound 2d (uB3LYP/6-311G* PCM CH₂Cl₂)

![Figure 28](image.png)

**Figure 28.** Optimized ground state geometry of radical cation of 2d (uB3LYP/6-311G* PCM CH₂Cl₂).

| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | -0.56144 | 1.18921 | 0.00009 |
| C       | -1.94859 | 1.33421 | 0.00008 |
| S       | -3.07397 | 0.00000 | 0.00001 |
| C       | -1.94859 | -1.33421 | -0.00007 |
| C       | -0.56144 | -1.18921 | -0.00009 |
| N       | 0.12513 | -0.00000 | -0.00000 |
|    |          |          |          |
|----|----------|----------|----------|
| C  | -2.35174 | -2.69817 | -0.00017 |
| C  | -1.28820 | -3.54822 | -0.00022 |
| S  | 0.24745  | -2.73177 | -0.00016 |
| S  | 0.24745  | 2.73177  | 0.00015  |
| C  | -1.28820 | 3.54822  | 0.00022  |
| C  | -2.35174 | 2.69817  | 0.00017  |
| C  | 1.57977  | 0.00000  | 0.00000  |
| C  | 2.25517  | 0.00083  | 1.21866  |
| C  | 3.64774  | -0.00084 | 1.21029  |
| C  | 4.34046  | -0.00000 | 0.00001  |
| C  | 3.64774  | 0.00084  | -1.21028 |
| C  | 2.25517  | 0.00083  | -1.21866 |
| H  | -3.38317 | -3.02397 | -0.00025 |
| H  | -1.30150 | -4.62782 | -0.00046 |
| H  | -1.30150 | 4.62782  | 0.00045  |
| H  | -3.38317 | 3.02397  | 0.00026  |
| H  | 1.70017  | -0.00137 | 2.14955  |
| H  | 4.18848  | -0.00151 | 2.14951  |
| H  | 5.42462  | 0.00000  | 0.00001  |
| H  | 4.18848  | 0.00151  | -2.14950 |
| H  | 1.70018  | 0.00137  | -2.14955 |

SCF Done: E(UB3LYP) = -1788.21155791 A.U. after 1 cycles
Zero-point correction= 0.191376 (Hartree/Particle)
Thermal correction to Energy= 0.205915
Thermal correction to Enthalpy= 0.206859
Thermal correction to Gibbs Free Energy= 0.147561
Sum of electronic and zero-point Energies= -1788.020182
Sum of electronic and thermal Energies= -1788.005643
Sum of electronic and thermal Enthalpies= -1788.004699
Sum of electronic and thermal Free Energies= -1788.063997
6.1.4.8 Reoptimization of compound 2d (uB3LYP/6-311G*)

Intra conformation of compound 2d in the gas phase (uB3LYP/6-311G*):

SCF Done: E(UB3LYP) = -1788.37510152 A.U. after 1 cycles
Zero-point correction= 0.190055 (Hartree/Particle)
Thermal correction to Energy= 0.204961
Thermal correction to Enthalpy= 0.205905
Thermal correction to Gibbs Free Energy= 0.145136
Sum of electronic and zero-point Energies= -1788.185047
Sum of electronic and thermal Energies= -1788.170141
Sum of electronic and thermal Enthalpies= -1788.169197
Sum of electronic and thermal Free Energies= -1788.229966

Intra conformation of compound 2d in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):

SCF Done: E(UB3LYP) = -1788.39792497 A.U. after 13 cycles

Extra conformation of compound 2d in the gas phase (uB3LYP/6-311G*):

SCF Done: E(UB3LYP) = -1788.37524185 A.U. after 1 cycles
Zero-point correction= 0.190467 (Hartree/Particle)
Thermal correction to Energy= 0.205047
Thermal correction to Enthalpy= 0.205991
Thermal correction to Gibbs Free Energy= 0.147102
Sum of electronic and zero-point Energies= -1788.184775
Sum of electronic and thermal Energies= -1788.170195
Sum of electronic and thermal Enthalpies= -1788.169251
Sum of electronic and thermal Free Energies= -1788.228139

Extra conformation of compound 2d in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):

SCF Done: E(UB3LYP) = -1788.39697559 A.U. after 13 cycles

Radical cation of compound 2d in the gas phase (uB3LYP/6-311G*):

SCF Done: E(UB3LYP) = -1788.15575888 A.U. after 1 cycles
Zero-point correction= 0.191255 (Hartree/Particle)
Thermal correction to Energy= 0.205812
Thermal correction to Enthalpy= 0.206756
Thermal correction to Gibbs Free Energy= 0.147528
Sum of electronic and zero-point Energies= -1787.964504
Sum of electronic and thermal Energies= -1787.949947
Sum of electronic and thermal Enthalpies= -1787.949003
Sum of electronic and thermal Free Energies= -1788.008231

Radical cation of compound 2d in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -1788.23106757 A.U. after 17 cycles

6.1.5.1 Computed xyz coordinates of compound 1 (B3LYP/6-311G* PCM CH₂Cl₂)

![Figure 38. Optimized ground state geometry of 1 (B3LYP/6-311G* PCM CH₂Cl₂).](image)

|   | C     | C     | C     | C     | C     | C     | C     | S     | C     | C     | C     | C     | C     | C     | C     | C     | C     | C     |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|   | -1.79337 | -1.35382 | 0.18137 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | -0.41726 | -1.23540 | -0.08761 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | 0.25073 | -0.00001 | 0.11397 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | -0.41724 | 1.23540 | -0.08761 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | -1.79335 | 1.35385 | 0.18137 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | -2.66168 | 0.00002 | 0.95043 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | 0.25898 | 2.37509 | -0.54768 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | -0.41323 | 3.58068 | -0.73737 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | -1.78115 | 3.67518 | -0.50141 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | -2.46839 | 2.55050 | -0.05032 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | -2.46844 | -2.55045 | -0.05032 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | -1.78122 | -3.67516 | -0.50140 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | -0.41330 | -3.58067 | -0.73737 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | 0.25894 | -2.37510 | -0.54767 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | 1.69187 | -0.00002 | 0.15687 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
SCF Done: E(RB3LYP) = -1146.86633720 A.U. after 1 cycles
Zero-point correction= 0.257429 (Hartree/Particle)
Thermal correction to Energy= 0.272493
Thermal correction to Enthalpy= 0.273438
Thermal correction to Gibbs Free Energy= 0.214229
Sum of electronic and zero-point Energies= -1146.608908
Sum of electronic and thermal Energies= -1146.593844
Sum of electronic and thermal Enthalpies= -1146.592900
Sum of electronic and thermal Free Energies= -1146.652108

6.1.5.2 Computed excitations of compound 1 (B3LYP/6-311G* PCM CH2Cl2)

Excited State 1: Singlet-A 3.5764 eV 346.67 nm f=0.0020 <S**2>=0.000
This state for optimization and/or second-order correction.

Total Energy, \( E(\text{TD-HF/TD-KS}) = -1146.73490644 \)

Copying the excited state density for this state as the 1-particle \( \text{RhoCl} \) density.

Excited State 2: Singlet-A  3.9114 eV  316.98 nm  f=0.0060  \(<S^2>\)=0.000  
72 -> 74  0.66769  
72 -> 76  -0.18158

Excited State 3: Singlet-A  4.0512 eV  306.04 nm  f=0.0340  \(<S^2>\)=0.000  
71 -> 73  -0.11785  
72 -> 74  0.19956  
72 -> 76  0.65578

Excited State 4: Singlet-A  4.0682 eV  304.76 nm  f=0.0280  \(<S^2>\)=0.000  
72 -> 75  0.68971

Excited State 5: Singlet-A  4.3064 eV  287.91 nm  f=0.0647  \(<S^2>\)=0.000  
71 -> 73  0.15342  
71 -> 76  -0.11557  
72 -> 77  0.66888

Excited State 6: Singlet-A  4.8647 eV  254.86 nm  f=0.4817  \(<S^2>\)=0.000  
71 -> 73  0.63595  
72 -> 76  0.13088  
72 -> 77  -0.16230  
72 -> 79  0.14033

Excited State 7: Singlet-A  4.9571 eV  250.12 nm  f=0.0939  \(<S^2>\)=0.000  
70 -> 73  0.11606
Excited State 8: Singlet-A 4.9814 eV  248.89 nm  f=0.0010  <S**2>=0.000
71 -> 73  -0.17084
71 -> 74  0.21204
71 -> 76  -0.17017
72 -> 79  0.61673

Excited State 9: Singlet-A 5.1136 eV  242.46 nm  f=0.0439  <S**2>=0.000
71 -> 74  0.65182
72 -> 79  -0.23231

Excited State 10: Singlet-A 5.2240 eV  237.34 nm  f=0.0450  <S**2>=0.000
71 -> 74  0.11747
71 -> 76  0.65402
72 -> 79  0.15669

6.1.5.3 Computed xyz coordinates of extra conformation of compound 1 (B3LYP/6-311G* PCM CH2Cl2)

![Computed xyz coordinates of extra conformation of compound 1](image)

**Figure 39.** Optimized ground state geometry of extra conformation of 1 (B3LYP/6-311G* PCM CH2Cl2).

|    | x       | y       | z       |
|----|---------|---------|---------|
| C  | 1.48026 | -1.34557| -0.52325|
| C  | 0.45906 | -1.20236| 0.42582 |
| N  | -0.31350| -0.00006| 0.44182 |
| C  | 0.45880 | 1.20237 | 0.42589 |
| Element | X    | Y    | Z    |
|---------|------|------|------|
| C       | 1.48003 | 1.34581 | -0.52311 |
| S       | 1.78509 | 0.00021 | -1.66228 |
| C       | 0.25639 | 2.21509 | 1.36718 |
| C       | 1.01353 | 3.38239 | 1.31675 |
| C       | 2.00720 | 3.53162 | 0.34861 |
| C       | 2.25654 | 2.50520 | -0.55818 |
| C       | 2.25693 | -2.50483 | -0.55844 |
| C       | 2.00779 | -3.53136 | 0.34830 |
| C       | 1.01422 | -3.38232 | 1.31655 |
| C       | 0.25690 | -2.21512 | 1.36709 |
| C       | -1.68693 | -0.00019 | 0.09146 |
| C       | -2.38976 | 1.20415 | -0.09677 |
| C       | -3.74004 | 1.19606 | -0.43412 |
| C       | -4.43412 | -0.00028 | -0.60081 |
| C       | -3.74016 | -1.19654 | -0.43342 |
| C       | -2.38983 | -1.20454 | -0.09605 |
| H       | -0.50543 | 2.08483 | 2.12755 |
| H       | 0.83640 | 4.16902 | 2.04202 |
| H       | 2.60546 | 4.43563 | 0.31445 |
| H       | 3.05415 | 2.59816 | -1.28723 |
| H       | 3.05451 | -2.59767 | -1.28754 |
| H       | 2.60618 | -4.43528 | 0.31402 |
| H       | 0.83726 | -4.16900 | 2.04181 |
| H       | -0.50485 | -2.08499 | 2.12757 |
| H       | -1.88329 | 2.15401 | 0.00676 |
| H       | -4.24883 | 2.14510 | -0.57243 |
| H       | -5.48690 | -0.00029 | -0.86125 |
| H       | -4.24897 | -2.14565 | -0.57113 |
| H       | -1.88350 | -2.15441 | 0.00806 |

SCF Done: $E_{(RB3LYP)} = -1146.86333621$ A.U. after 1 cycles
Zero-point correction= 0.257302 (Hartree/Particle)
Thermal correction to Energy= 0.272334
Thermal correction to Enthalpy= 0.273278
Thermal correction to Gibbs Free Energy= 0.214246
Sum of electronic and zero-point Energies= -1146.606034
Sum of electronic and thermal Energies= -1146.591002
Sum of electronic and thermal Enthalpies= -1146.590058
Sum of electronic and thermal Free Energies= -1146.649090

6.1.5.4 Computed xyz coordinates of radical cation 1+ of compound 1 (uB3LYP/6-311G* PCM CH2Cl2)

![Figure 40. Optimized ground state geometry of 1 (uB3LYP/6-311G* PCM CH2Cl2).](image)

|    | x       | y       | z       |
|----|---------|---------|---------|
| C  | -1.82928| -1.36070| -0.00007|
| C  | -0.41488| -1.23827| -0.00003|
| N  | 0.22657 | -0.00001| 0.00001 |
| C  | -0.41482| 1.23828 | -0.00004|
| C  | -1.82920| 1.36079 | -0.00001|
| S  | -2.91181| 0.00007 | 0.00005 |
| C  | 0.34754 | 2.42904 | -0.00012|
| C  | -0.26671| 3.66346 | -0.00014|
| C  | -1.66647| 3.77127 | -0.00008|
| C  | -2.43624| 2.62690 | -0.00002|
| C  | -2.43639| 2.62678 | -0.00014|
| C  | -1.66668| -3.77120| -0.00014|
| C  | -0.26691| -3.66346| -0.00005|
| C  | 0.34741 | -2.42908| -0.00000|
| C     | 1.68385 | -0.00004 | 0.00006 |
| C     | 2.36260 | -0.00006 | 1.21529 |
| C     | 3.75600 | -0.00008 | 1.20906 |
| C     | 4.45104 | -0.00009 | 0.00017 |
| C     | 3.75610 | -0.00008 | -1.20877|
| C     | 2.36270 | -0.00005 | -1.21511|
| H     | 1.42558 | 2.37367  | -0.00018|
| H     | 0.34562 | 4.55725  | -0.00020|
| H     | -2.14207| 4.74442  | -0.00009|
| H     | -3.51828| 2.69356  | 0.00000 |
| H     | -3.51843| -2.69338 | -0.00020|
| H     | -2.14233| -4.74431 | -0.00019|
| H     | 0.34536 | -4.55728 | -0.00003|
| H     | 1.42545 | -2.37377 | 0.00006 |
| H     | 1.80898 | -0.00005 | 2.14730 |
| H     | 4.29538 | -0.00010 | 2.14931 |
| H     | 5.53526 | -0.00012 | 0.00022 |
| H     | 4.29555 | -0.00008 | -2.14898|
| H     | 1.80915 | -0.00003 | -2.14716|

SCF Done: E(UB3LYP) = -1146.68068878 A.U. after 1 cycles
Zero-point correction= 0.258680 (Hartree/Particle)
Thermal correction to Energy= 0.273666
Thermal correction to Enthalpy= 0.274610
Thermal correction to Gibbs Free Energy= 0.215260
Sum of electronic and zero-point Energies= -1146.422008
Sum of electronic and thermal Energies= -1146.407023
Sum of electronic and thermal Enthalpies= -1146.406079
Sum of electronic and thermal Free Energies= -1146.465429
6.1.5.5 Reoptimization of compound 1 (uB3LYP/6-311G*)

Intra conformation of compound 1 in the gas phase (uB3LYP/6-311G*):

SCF Done:  \( E(\text{UB3LYP}) = -1146.85995451 \) A.U. after 1 cycles
Zero-point correction= 0.257455 (Hartree/Particle)
Thermal correction to Energy= 0.272510
Thermal correction to Enthalpy= 0.273454
Thermal correction to Gibbs Free Energy= 0.214283
Sum of electronic and zero-point Energies= -1146.602499
Sum of electronic and thermal Energies= -1146.587445
Sum of electronic and thermal Enthalpies= -1146.586500
Sum of electronic and thermal Free Energies= -1146.645671

Intra conformation of compound 1 in \( \text{CH}_2\text{Cl}_2 \) (uB3LYP/6-311G* SMD \( \text{CH}_2\text{Cl}_2 \)):

SCF Done:  \( E(\text{UB3LYP}) = -1146.88550803 \) A.U. after 13 cycles

Extra conformation of compound 1 in the gas phase (uB3LYP/6-311G*):

SCF Done:  \( E(\text{UB3LYP}) = -1146.85695873 \) A.U. after 1 cycles
Zero-point correction= 0.257345 (Hartree/Particle)
Thermal correction to Energy= 0.272359
Thermal correction to Enthalpy= 0.273303
Thermal correction to Gibbs Free Energy= 0.214383
Sum of electronic and zero-point Energies= -1146.602499
Sum of electronic and thermal Energies= -1146.584599
Sum of electronic and thermal Enthalpies= -1146.583655
Sum of electronic and thermal Free Energies= -1146.642576

Extra conformation of compound 1 in \( \text{CH}_2\text{Cl}_2 \) (uB3LYP/6-311G* SMD \( \text{CH}_2\text{Cl}_2 \)):

SCF Done:  \( E(\text{UB3LYP}) = -1146.88245909 \) A.U. after 13 cycles

Radical cation of compound 1 in the gas phase (uB3LYP/6-311G*):

SCF Done:  \( E(\text{UB3LYP}) = -1146.62706133 \) A.U. after 1 cycles
Zero-point correction= 0.258526 (Hartree/Particle)
Thermal correction to Energy= 0.273567
Thermal correction to Enthalpy= 0.274511
Thermal correction to Gibbs Free Energy= 0.214761
Sum of electronic and zero-point Energies= -1146.368535
Sum of electronic and thermal Energies= -1146.353495
Sum of electronic and thermal Enthalpies= -1146.352550
Sum of electronic and thermal Free Energies= -1146.412300

Radical cation of compound 1 in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -1146.70557160  A.U. after  17 cycles

6.1.6.1 Computed xyz coordinates of compound 2e (B3LYP/6-311G* PCM CH₂Cl₂)

Figure 43. Optimized ground state geometry of 2e (B3LYP/6-311G* PCM CH₂Cl₂).

| Atom | X-Coordinate | Y-Coordinate | Z-Coordinate |
|------|--------------|--------------|--------------|
| C    | 2.05050      | -0.78842     | 0.19107      |
| C    | 0.72091      | -1.06143     | -0.01696     |
| N    | -0.28267     | -0.08549     | 0.19445      |
| C    | 0.09047      | 1.25138      | 0.04332      |
| C    | 1.35509      | 1.75472      | 0.21189      |
| S    | 2.67087      | 0.73248      | 0.86940      |
| S    | -0.99607     | 2.48907      | -0.56097     |
| C    | 0.28416      | 3.67512      | -0.53170     |
| C    | 1.46765      | 3.13604      | -0.12875     |
| S    | 3.05933      | -2.13879     | -0.24280     |
| C    | 1.66525      | -3.08951     | -0.64961     |
| C    | 0.50386      | -2.39153     | -0.49920     |
| C    | -1.67398     | -0.44953     | 0.19150      |
| C    | -2.35004     | -0.66319     | -1.01242     |
| C    | -3.70071     | -1.00778     | -0.99604     |
| C    | -4.37462     | -1.13697     | 0.21771      |
| C    | -3.69778     | -0.92226     | 1.41809      |
C  -2.34723  -0.57968  1.40684  
H   0.06026   4.69931  -0.78912  
H   2.38710   3.70160  -0.04226  
H  -1.79252  -4.10927  -0.98068  
H  -0.47196  -2.80530  -0.71373  
H  -1.81892  -0.56023  -1.95241  
H  -4.22466  -1.17436  -1.93110  
H  -5.42577  -1.40494   0.22806  
H  -4.21979  -1.02293   2.36358  
H  -1.80733  -0.41135   2.33200

SCF Done:  E(RB3LYP) = -1788.38209752  A.U. after  1 cycles
Zero-point correction= 0.190206 (Hartree/Particle)
Thermal correction to Energy= 0.205024
Thermal correction to Enthalpy= 0.205968
Thermal correction to Gibbs Free Energy= 0.146165
Sum of electronic and zero-point Energies= -1788.191892
Sum of electronic and thermal Energies= -1788.177073
Sum of electronic and thermal Enthalpies= -1788.176129
Sum of electronic and thermal Free Energies= -1788.235933

6.1.6.2 Computed xyz coordinates of radical cation 2e⁺ of compound 2e (uB3LYP/6-311G* PCM CH₂Cl₂)

Figure 44. Optimized ground state geometry of radical cation of 2e (uB3LYP/6-311G* PCM CH₂Cl₂).

C  -2.10316  -0.72281   0.00003  
C  -0.74228  -1.03592  -0.00003
| Element | X   | Y    | Z     |
|---------|-----|------|-------|
| N       | 0.25592 | -0.07293 | -0.00005 |
| C       | -0.05695 | 1.25968 | -0.00001 |
| C       | -1.34138 | 1.80702 | 0.00003 |
| S       | -2.80694 | 0.86334 | 0.00002 |
| S       | 1.16307 | 2.50453 | -0.00004 |
| C       | -0.06967 | 3.73317 | -0.00000 |
| C       | -1.33389 | 3.22903 | 0.00003 |
| S       | -3.08622 | -2.15211 | 0.00002 |
| C       | -1.66774 | -3.15335 | -0.00006 |
| C       | -0.50857 | -2.44491 | -0.00007 |
| C       | 1.65160 | -0.48042 | -0.00001 |
| C       | 2.30023 | -0.67478 | 1.21733 |
| C       | 3.63625 | -1.06879 | 1.20975 |
| C       | 4.30145 | -1.26530 | 0.00005 |
| C       | 3.63633 | -1.06875 | -1.20967 |
| C       | 2.30030 | -0.67474 | -1.21731 |
| H       | 0.23172 | 4.76994 | 0.00003 |
| H       | -2.22825 | 3.83762 | 0.00008 |
| H       | -1.78788 | -4.22635 | -0.00007 |
| H       | 0.47281 | -2.89568 | -0.00009 |
| H       | 1.76850 | -0.52113 | 2.14920 |
| H       | 4.15402 | -1.22325 | 2.14937 |
| H       | 5.34103 | -1.57316 | 0.00009 |
| H       | 4.15414 | -1.22317 | -2.14928 |
| H       | 1.76863 | -0.52106 | -2.14921 |

SCF Done:  E(UB3LYP) = -1788.21126114  A.U. after  1 cycles
Zero-point correction= 0.191446 (Hartree/Particle)
Thermal correction to Energy= 0.205963
Thermal correction to Enthalpy= 0.206908
Thermal correction to Gibbs Free Energy= 0.147814
Sum of electronic and zero-point Energies= -1788.019815
Sum of electronic and thermal Energies= -1788.005298
Sum of electronic and thermal Enthalpies= -1788.004353
Sum of electronic and thermal Free Energies= -1788.063447

6.1.6.3 Reoptimization of compound 2e (UB3LYP/6-311G*)
Intra conformation of compound 2e in the gas phase (UB3LYP/6-311G*):
SCF Done: E(UB3LYP) = -1788.37547801 A.U. after 1 cycles
Zero-point correction= 0.190261 (Hartree/Particle)
Thermal correction to Energy= 0.205075
Thermal correction to Enthalpy= 0.206019
Thermal correction to Gibbs Free Energy= 0.146055
Sum of electronic and zero-point Energies= -1788.185217
Sum of electronic and thermal Energies= -1788.170403
Sum of electronic and thermal Enthalpies= -1788.169459
Sum of electronic and thermal Free Energies= -1788.229423

Intra conformation of compound 2e in CH₂Cl₂ (UB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -1788.39792198 A.U. after 14 cycles
Radical cation of compound 2e in the gas phase (UB3LYP/6-311G*):
SCF Done: E(UB3LYP) = -1788.15514272 A.U. after 1 cycles
Zero-point correction= 0.191406 (Hartree/Particle)
Thermal correction to Energy= 0.205941
Thermal correction to Enthalpy= 0.206885
Thermal correction to Gibbs Free Energy= 0.147613
Sum of electronic and zero-point Energies= -1787.963737
Sum of electronic and thermal Energies= -1787.949202
Sum of electronic and thermal Enthalpies= -1787.948258
Sum of electronic and thermal Free Energies= -1788.007530

Radical cation of compound 2e in CH₂Cl₂ (UB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -1788.23037540 A.U. after 18 cycles

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6.1.7.1 Computed xyz coordinates of compound 2f (B3LYP/6-311G* PCM CH₂Cl₂)

Figure 41. Optimized ground state geometry of 2f (B3LYP/6-311G* PCM CH₂Cl₂).

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 2.18278   | -0.70727  | 0.12766   |
| C       | 0.77898   | -1.01075  | 0.00606   |
| N       | -0.21644  | -0.02885  | 0.17968   |
| C       | 0.12728   | 1.31392   | 0.02375   |
| C       | 1.38240   | 1.85257   | 0.13921   |
| S       | 2.78493   | 0.88356   | 0.66015   |
| C       | 2.97971   | -1.79059  | -0.08904  |
| S       | 2.05024   | -3.21966  | -0.40732  |
| C       | 0.56199   | -2.33092  | -0.28243  |
| S       | -1.03777  | 2.53675   | -0.45022  |
| C       | 0.20076   | 3.76668   | -0.44254  |
| C       | 1.42288   | 3.25356   | -0.13470  |
| C       | -1.60198  | -0.41676  | 0.16858   |
| C       | -2.25843  | -0.65831  | -1.04024  |
| C       | -3.60160  | -1.03084  | -1.03378  |
| C       | -4.28480  | -1.16230  | 0.17468   |
| C       | -3.62533  | -0.92194  | 1.37990   |
| C       | -2.28236  | -0.55072  | 1.37909   |
| H       | 4.05760   | -1.83898  | -0.05188  |
| H       | -0.37972  | -2.83505  | -0.42849  |
| H       | -0.07029  | 4.78991   | -0.65346  |
| H       | 2.32710   | 3.84740   | -0.08178  |
| H       | -1.71836  | -0.55403  | -1.97485  |
| H       | -4.11277  | -1.21725  | -1.97214  |
| H       | -5.33022  | -1.45201  | 0.17718   |
| H       | -4.15500  | -1.02427  | 2.32090   |
| H       | -1.75545  | -0.36212  | 2.30782   |
SCF Done: $E_{(RB3LYP)} = -1788.38728250$ A.U. after 1 cycles
Zero-point correction= 0.190179 (Hartree/Particle)
Thermal correction to Energy= 0.204969
Thermal correction to Enthalpy= 0.205913
Thermal correction to Gibbs Free Energy= 0.146212
Sum of electronic and zero-point Energies= -1788.197103
Sum of electronic and thermal Energies= -1788.182313
Sum of electronic and thermal Enthalpies= -1788.181369
Sum of electronic and thermal Free Energies= -1788.241071

6.1.7.2 Computed xyz coordinates of radical cation 2f$^+$ of compound 2f (uB3LYP/6-311G$^*$ PCM CH$_2$Cl$_2$)

Figure 42. Optimized ground state geometry radical cation of 2f (uB3LYP/6-311G$^*$ PCM CH$_2$Cl$_2$).

|      |        |        |        |
|------|--------|--------|--------|
| C    | 2.19913| -0.70269| 0.00007|
| C    | 0.78646| -0.99895| -0.00004|
| N    | -0.20065| -0.01099| -0.00002|
| C    | 0.11782| 1.30771| -0.00009|
| C    | 1.41468| 1.85344| 0.00000|
| S    | 2.87345| 0.91900| -0.00006|
| C    | 2.96781| -1.83332| 0.00012|
| S    | 1.99509| -3.25366| 0.00004|
| C    | 0.53758| -2.35190| -0.00004|
| S    | -1.10298| 2.55888| -0.00007|
| C    | 0.13907| 3.78086| 0.00004|
| C    | 1.40290| 3.27364| 0.00006|
| C    | -1.59860| -0.41187| -0.00002|
C    -2.24694  -0.60474  -1.21772
C    -3.58481  -0.99222  -1.20978
C    -4.25085  -1.18508   0.00007
C    -3.58482  -0.99196   1.20986
C    -2.24694  -0.60449   1.21770
H    4.04450  -1.90808   0.00014
H    -0.41656  -2.85299  -0.00017
H    -0.15673   4.81944  -0.00003
H    2.29685   3.88279   0.00013
H    -1.71428  -0.45382  -2.14943
H    -4.10346  -1.14409  -2.14931
H    -5.29204  -1.48741   0.00008
H    -4.10345  -1.14362   2.14945
H    -1.71426  -0.45337   2.14937

SCF Done:  E(UB3LYP) = -1788.20952914 A.U. after 1 cycles
Zero-point correction= 0.191196 (Hartree/Particle)
Thermal correction to Energy= 0.205734
Thermal correction to Enthalpy= 0.206679
Thermal correction to Gibbs Free Energy= 0.147360
Sum of electronic and zero-point Energies= -1788.018333
Sum of electronic and thermal Energies= -1788.003795
Sum of electronic and thermal Enthalpies= -1788.002851
Sum of electronic and thermal Free Energies= -1788.062169

6.1.7.3 Reoptimization of compound 2f (uB3LYP/6-311G*)
Intra conformation of compound 2f in the gas phase (uB3LYP/6-311G*):
SCF Done:  E(UB3LYP) = -1788.38072441 A.U. after 1 cycles
Zero-point correction= 0.190287 (Hartree/Particle)
Thermal correction to Energy= 0.205059
Thermal correction to Enthalpy= 0.206003
Thermal correction to Gibbs Free Energy= 0.146321
Intra conformation of compound 2f in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):

SCF Done:  E(UB3LYP) = -1788.40300796  A.U. after  13 cycles

Radical cation of compound 2f in the gas phase (uB3LYP/6-311G*):

SCF Done:  E(UB3LYP) = -1788.15341717  A.U. after  1 cycles
Zero-point correction= 0.191177  (Hartree/Particle)
Thermal correction to Energy= 0.205698
Thermal correction to Enthalpy= 0.206643
Thermal correction to Gibbs Free Energy= 0.147418
Sum of electronic and zero-point Energies= -1787.962240
Sum of electronic and thermal Energies= -1787.947719
Sum of electronic and thermal Enthalpies= -1787.946775
Sum of electronic and thermal Free Energies= -1788.006000

Radical cation of compound 2f in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):

SCF Done:  E(UB3LYP) = -1788.22904361  A.U. after  19 cycles
6.2 DFT calculation of the redox potentials of compounds 1 and 2

The calculation of the redox potentials (Table 6) was carried out by adapting a literature procedure (equation 1) based on DFT methods.\[12\]

\[
E_{\text{redox}} = \frac{\Delta G_{\text{redox(solv)}}}{-F} = \frac{\Delta G_{\text{redox(gas)}} + \Delta G_{\text{solv(ox)}} - \Delta G_{\text{solv(red)}}}{-F}
\]  
(equation 1)

\( E_{\text{redox}} \) \hspace{1cm} redox potential vs. vacuum
\( \Delta G_{\text{redox(solv)}} \) \hspace{1cm} free enthalpy of oxidation in solution/gas phase
\( \Delta G_{\text{solv(ox/red)}} \) \hspace{1cm} free enthalpy of solvation of the oxidized/reduced compound
\( F \) \hspace{1cm} Faraday constant (23.06 kcal mol\(^{-1}\)V\(^{-1}\))

\( \Delta G_{\text{solv(gas)}} \), \( \Delta G_{\text{solv(solv)}} \) and \( \Delta G_{\text{redox(gas)}} \) were calculated from the values of the free enthalpies obtained from the geometry optimizations given in chapter 6.1 (uB3LYP/6-311G*). The SMD solvation model\[10\] with dichloromethane as a solvent was applied to determine the solvation enthalpies, since all experimental determined oxidation potentials were measured in dichloromethane solutions.

**Table 6.** Calculated \( \Delta G_{\text{solv}}, \Delta G_{\text{redox}} \) and \( E_{\text{redox,0/+1}} \) of intrac conformation of compounds 1 and 2 (uB3LYP/6-311G* SMD CH\(_2\)Cl\(_2\)).

| Compound | \( \Delta G_{\text{redox(gas)}} \) [kcal/mol] | \( \Delta G_{\text{solv(red)}} \) [kcal/mol] | \( \Delta G_{\text{solv(ox)}} \) [kcal/mol] | \( \Delta G_{\text{redox(solv)}} \) [kcal/mol] | \( E_{\text{redox,0/+1}} \) vs. vacuum [V] |
|----------|--------------------------------|
| 1        | 146.3447 | -16.0244 | -49.2330 | 113.1361 | 4.9093 |
| 2a       | 139.5717 | -13.8269 | -46.9969 | 106.4017 | 4.6171 |
| 2b       | 143.9494 | -13.6044 | -47.2048 | 110.3491 | 4.7884 |
| 2c       | 149.8857 | -13.4911 | -47.4498 | 115.9270 | 5.0304 |
| 2d       | 139.0475 | -14.3124 | -47.2253 | 106.0438 | 4.6055 |
| 2e       | 139.1470 | -14.0744 | -47.1777 | 106.0438 | 4.6016 |
| 2f       | 143.2299 | -13.9738 | -47.4246 | 109.7792 | 4.7637 |
For a linear correlation of the measured first oxidation potential $E_{0+/1}^{exp}$ with the calculated first oxidation potential $E_{0+/1}^{cal}$ of the compounds 1 and 2 in their intra conformations in the gas-phase, see figure 45.

![Figure 45](image)

Figure 45. Linear correlation of the measured first oxidation potential $E_{0+/1}^{exp}$ (0.1 M [Bu$_4$N][PF$_6$], $v = 100$ mV/s. Pt-working, Ag/AgCl-reference and Pt-counter electrode, [Me$_{10}$Fc]/[Me$_{10}$Fc]$^+$ as an internal standard) and the calculated first oxidation potential $E_{0+/1}^{cal}$ (vs. vacuum, uB3LYP/6-311G*) of the compounds 1 and 2 in their intra conformations in the gas-phase.

The redox potentials were also calculated for the extra conformers revealing a poorer correlation with the experimental results (Table 7, Figure 46), which indicates that the redox behavior of the dithienothiazines 2 is dominated by the intra conformations respectively.

Table 7. Calculated $\Delta G_{solv}$, $\Delta G_{redox}$ and $E_{redox,0+/1}$ of extra conformations of compounds 1 and 2 (uB3LYP/6-311G* SMD CH$_2$Cl$_2$).

| Compound (extra conf.) | $\Delta G_{redox}^{gas}$ [kcal/mol] | $\Delta G_{solv}^{red}$ [kcal/mol] | $\Delta G_{solv}^{ox}$ [kcal/mol] | $\Delta G_{redox}^{solv}$ [kcal/mol] | $E_{redox,0+/1}$ vs. vacuum [V] |
|------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|-------------------------------|
| 1                      | 144.4034                         | -15.9910                         | -49.2330                         | 111.1614                         | 4.8236                        |
| 2a                     | 138.6395                         | -13.4095                         | -46.9969                         | 105.0521                         | 4.5585                        |
| 2b                     | 140.9936                         | -13.6331                         | -47.2048                         | 107.4220                         | 4.6614                        |
| 2c                     | 145.5398                         | -13.6875                         | -47.4498                         | 111.7775                         | 4.8504                        |
| 2d                     | 137.9027                         | -13.6290                         | -47.2253                         | 104.3064                         | 4.5262                        |
Figure 46. Linear correlation of the measured first oxidation potential $E_{0+/1}^{\text{exp}}$ (0.1 M [Bu4N][PF6], $\nu = 100$ mV/s, Pt-working, Ag/AgCl-reference and Pt-counter electrode, [Me10Fc]/[Me10Fc]$^+$ as an internal standard) and the calculated first oxidation potential $E_{0+/1}^{\text{cal}}$ (vs. vacuum, uB3LYP/6-311G*, SMD CH2Cl2) of the compounds 1 and 2 in their extra conformations.

From the calculated differences of the free enthalpies of the extra and intra conformers $\Delta G_{\text{extra-intra}}$ (see chapter 6.1) we calculated the equilibrium mole fraction of the extra and intra conformers assuming a Boltzmann distribution. Given the mole fractions, we calculated the effective redox potentials consisting of the oxidation potentials of both conformers further suggesting, that the intra conformers dominate the electrochemical properties at least in CV experiments (Figure 47).

Figure 47. Linear correlation of the measured first oxidation potential $E_{0+/1}^{\text{exp}}$ (0.1 M [Bu4N][PF6], $\nu = 100$ mV/s, Pt-working, Ag/AgCl-reference and Pt-counter electrode, [Me10Fc]/[Me10Fc]$^+$ as an internal standard) and the calculated first oxidation potential $E_{0+/1}^{\text{cal}}$ (vs. vacuum, uB3LYP/6-311G*, SMD CH2Cl2) of the compounds 1 and 2 in their intra and extra conformations in a Boltzmann distribution.
7 References

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