Electronic Supporting Information

Thermal conversion of a pyridine-bridged bisdithiazolyl radical to a zwitterionic bisdithiazolopyridone

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Contents

Section S1 Synthetic Procedures and Instrumental Methods.

General methods and procedures The solvents acetonitrile (MeCN), dichloroethane (DCE), dichloromethane (DCM), methanol, isopropanol and diethyl ether were of at least reagent grade. MeCN was dried by distillation from P_2O_5 and/or CaH_2, methanol by distillation from magnesium turnings, and both DCE and DCM by distillation from P_2O_5. All reactions were performed under an atmosphere of dry nitrogen. Melting points are uncorrected. Fractional sublimations were performed in an ATS series 3210 three-zone tube furnace, mounted horizontally, and linked to a series 1400 temperature control system. Infrared spectra (Nujol mulls, KBr optics) were recorded on a Nicolet Avatar FTIR spectrometer at 2 cm^{-1} resolution. ^1H spectra were run on a Bruker Avance 300 MHz NMR spectrometer and low resolution Electro-Spray Ionization (ESI) mass spectra were run on a Micromass Q-TOF Ultima Global LC/MS/MS system. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ 85018.

Preparation of 4-methoxy-2,6-difluoropyridine 6 A solution of 2,4,6-trifluoropyridine (13.3 g, 0.10 mol) in 20 mL anhydrous methanol was added dropwise to a solution of sodium methoxide prepared by dissolving freshly cut sodium (2.30 g, 0.10 mol) in 100 mL methanol. The solution was stirred under N_2 for 1 h, and the solvent removed by rotary evaporation to leave a white paste. Diethyl ether (200 mL) was added, and the precipitate of sodium fluoride (3.9 g, 0.093 mol) was filtered off. The solvent was evaporated to leave a colorless oil which was distilled to give 4-methoxy-2,6-difluoropyridine **6** (10.1 g, 0.070 mol, 70 %) as a colorless oil, bp 70-72 °C /10 Torr. ^1H NMR (δ, $CDCl_3$): 6.28 (s, 2H, aromatic), 3.87 (s, 3H, OMe). Anal. Calcd for $C_6H_5F_2NO$: C, 49.66; H, 3.47; N, 9.65 %. Found: C, 48.79; H, 3.68; N, 9.77 %.

Preparation of *N*-methyl-4-methoxy-2,6-difluoropyridinium Triflate 7 A solution of 4-methoxy-2,6-difluoropyridine (5.00 g, 34.5 mmol) and methyl triflate (7.35 g, 44.8 mmol) in 30 mL DCE was left to stir under N_2 for 16 h. Diethyl ether (100 mL) was added and the resulting white precipitate of *N*-methyl-4-methoxy-2,6-difluoropyridinium triflate was filtered off, washed with 2 × 50 mL ether and dried in vacuo. Yield 10.0 g, 32.4 mmol, 94 %. Recrystallization from DCE/MeCN afforded colorless needles, mp 79-80 °C. ^{1}H NMR (δ, CD_3CN): 7.17 (d, 2H, *J* = 4.8Hz, aromatic), 4.11 (s, 3H, NMe), 3.84 (t, 3H, *J* = 2.7Hz, OMe). Anal. Calcd for $C_8H_8F_5NO_4S$: C, 31.07; H, 2.61; N, 4.53 %. Found: C, 31.21; H, 2.89; N, 4.72 %.

Preparation of *N*-methyl-4-methoxy-2,6-diaminopyridinium Triflate 8 Ammonia gas was bubbled into a solution of *N*-methyl-4-methoxy-2,6-difluoropyridinium triflate **7** (10.0 g, 32.4 mmol) in 120 mL anhydrous MeCN for 15 min. The vessel (a glass bomb) was then sealed and heated at 50 °C for 16 h. The vessel was cooled to room temperature, opened to vent, and the vessel reheated to 100 °C to discharge excess ammonia. The reaction mixture was filtered to remove NH_4F (2.3 g), and the solvent was removed from the filtrate to afford *N*-methyl-4-methoxy-2,6-diaminopyridinium triflate **8** as a white solid that was recrystallized from isopropanol, mp 174-176°C . Yield 8.3 g (27.3 mmol, 84%). ^{1}H NMR (δ, CD_3CN): 5.85 (s, 4H, broad NH_2), 5.82 (s, 2H, aromatic), 3.80 (s, 3H, NMe), 3.36 (s, 3H, OMe). Anal. Calcd for $C_8H_{12}F_3N_3O_4S$: C, 31.68; H, 3.99; N, 13.86 %. Found: C, 32.00; H, 4.04; N, 14.05 %.

Preparation of 8-Methoxy-4-methyl-4H-bis[1,2,3]dithiazolo[4,5-b:5',4'-e]pyridin-2-ium Triflate [4a][OTf] A solution of S_2Cl_2 (18.0 g, 0.133 mol) in 20 mL DCE was added dropwise to a slurry of *N*-methyl-4-methoxy-2,6-diaminopyridinium triflate **7** (8.00 g, 26.4 mmol) in a mixture of 40 mL MeCN and 20 mL DCE, and the mixture set to reflux under N_2 for 4 h. The mixture was cooled to RT for 1 h, then at −20 °C for 3 h. The sparkling red microcrystalline solid was filtered off, washed with 2 × 50 mL DCE, 50 mL CS_2, 50 mL DCE, and pumped dry. Yield 8.3 g. This solid was boiled into 200 mL MeCN, and the solution filtered and the filtrate boiled down to 75 mL. Red crystals of [**4a**][OTf] appeared immediately on cooling to RT. The flask was cooled to −20 °C overnight, and the product collected by filtration and washed with DCE. Yield 5.23 g (12.3 mmol, 47 %), dec > 225 °C. ^{1}H NMR (δ, CD_3CN): 4.01 (s, 3H, OMe), 3.61 (s, 3H, NMe). IR: 1523 (m), 1428 (m), 1402 (w), 1361 (m), 1271 (s), 1246 (s), 1224 (s), 1158 (m), 1055 (w), 1028 (s), 856 (m), 797 (s), 682 (s), 668 (w), 638 (s), 517 (w), 481 (m) cm^{-1}. Anal. Calcd for $C_8H_6F_3N_3O_4S_5$: C, 22.58; H, 1.42; N, 9.88 %. Found: C, 22.60; H, 1.55; N, 10.03 %. Addition of $[BzEt_3N][Cl]$ to a solution of [**4a**][OTf] in MeCN produced a blue-black precipitate of the corresponding chloride salt

[**4a**][Cl]. Treatment of the latter with a stoichiometric quantity of $AgSbF_6$ in MeCN afforded a deep red solution of the hexafluoroantimonate salt [**4a**][SbF_6], which was recrystallized from DCE for analytical and crystallographic purposes. IR: 1524 (m), 1407 (m), 1358 (m), 1219 (w), 1203 (w), 1138 (w), 1057 (w), 927 (w), 858 (w), 794 (s), 681 (s), 659 (vs), 476 (m) cm^{-1}.

Preparation of 8-methoxy-4-methyl-4H-bis[1,2,3]dithiazolo[4,5-b:5',4'-e]pyridin-3-yl 4a TDAE (300 μL, 260 mg, 1.3 mmol) was injected by syringe into a slurry of [MeOBPMe][OTf] (851 mg, 2.00 mmol) in 25 mL of bubble degassed MeCN held in EtOH at −20 °C. The TDAE dissolved over a period of minutes, to produce a dark grey solid in a red solution. After 30 min, the solid material, crude 8-methoxy-4-methyl-4H-bis[1,2,3]dithiazolo[4,5-b:5',4'-e]pyridin-3-yl **4a**, was filtered off, washed with 3 × 15 mL MeCN, and dried in vacuo. Yield 0.470 g, 1.70 mmol, 85%. IR: 1499 (w), 1241 (s), 1208 (m), 1115 (m), 1053 (m), 971 (w), 914 (w), 817 (w), 772 (m), 656 (m), 609 (w) cm^{-1}.

Thermal Conversion of 4a to 9 and 5a A slurry of **4a** (0.470 g, 1.70 mmol) in 10 mL of degassed (4 freeze-pump-thaw cycles) DCE was warmed to 50 °C. The solid dissolved to afford a dark green solution that darkened and turned red within a few minutes. A heavy dark brown precipitate was also formed. After 20 min the mixture was allowed to cool to room temperature. After 36 hr the brown solid, the intermediate radical **9**, was filtered off, washed with 20 mL DCE and 2 × 20 mL MeCN, and dried in vacuo. Yield, 330 mg (0.61mol, 72% for **9** from **4a**). IR: 1604 (m), 1522 (s), 1353 (s), 1269 (s), 1212 (m), 1196 (w), 1129 (w), 1058 (s), 1039 (s), 863 (m), 796 (m), 719 (w), 682 (m), 624 (w), 572 (w) cm^{-1}. Crude **9** (330 mg, 0.61 mol) was heated overnight at 130 °C/10^{-3} Torr. The resulting black solid, crude bis-1,2,3-dithiazolo-*N*-methyl-pyridone **5a** (300 mg, 1.1 mmol, 67 % from **4a**) was purified by sublimation in a tube furnace along a temperature gradient of 200−140 °C /10^{-3} Torr to afford purple blocks, mp > 250 °C. IR: 1509 (s), 1462 (s), 1392 (s), 1383 (s), 1366 (s), 1212 (m), 1054 (w), 862 (m), 853 (m), 791 (s), 724 (s), 676 (s), 635 (w), 857 (m), 486 (m), 475 9 (w), 445 (m) cm^{-1}. Anal. Calcd for $C_6H_3N_3OS$: C, 27.57; H, 1.16; N, 16.08 %. Found: C, 27.60; H, 1.31; N, 16.14 %.

Cyclic Voltammetry Cyclic voltammetry was performed using a PINE Bipotentiostat, Model AFCClBP1, with scan rates of 50-100 mV s^{-1} on solutions of [**4a**][OTf] in CH_3CN (dried by distillation from P_2O_5 and CaH_2) containing 0.1 M tetra-*n*-butyl-ammonium hexafluorophosphate. Potentials were scanned with respect to the quasi-reference electrode in a single compartment cell fitted with Pt electrodes and referenced to the Fc/Fc^+ couple of ferrocene at 0.38 V *vs* SCE.[1] The E_{pa}-E_{pc} separation of the reversible couples were within 10 % of that of the Fc/Fc^+ couple.

EPR Spectra X-Band EPR spectra were recorded at ambient temperature using a Bruker EMX-200 spectrometer; samples of the radicals were dissolved in degassed CH_2Cl_2. Hyperfine coupling constants were obtained by spectral simulation using Simfonia[2] and WinSim.

X-ray Measurements Needles of [**4a**][SbF_6] and **5a** were glued to glass fibers with epoxy. X-ray data were collected using omega scans with a Bruker APEX I CCD detector on a D8 3-circle goniometer and Mo K_α ($\lambda = 0.71073$ Å) radiation. The data were scanned using Bruker's SMART program and integrated using Bruker's SAINT software.[3] The structures were solved by direct methods using SHELXS-90[4] and refined by least-squares methods on F^2 using SHELXL-97[5] incorporated in the SHELXTL[6] suite of programs.

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[1] R. T. Boeré, K. H. Moock and M. Parvez, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1589.

[2] WinEPR Simfonia, version 1.25; Bruker Instruments, Inc., Billerica, MA, 1996.

[3] SAINT, version 6.22 Bruker Advanced X-ray Solutions, Inc., Madison, WI, 2001.

[4] Sheldrick, G. M. SHELXS-90. *Acta Crystallogr. A* 1990, **46**, 467.

[5] Sheldrick, G. M. SHELXL-97. Program for the Refinement of Crystal Structures, University of Gottingen, Gottingen, Germany, 1997.

[6] SHELXTL, VERSION 6.12 Program Library for Structure Solution and Molecular Graphics, Bruker Advanced X-ray Solutions, Inc., Madison, WI, 2001.

Section S2 Gaussian 09[7] Archive Files.

1. Radical **4a**, PCM based UB3LYP/6-311G(d,p) full optimization.

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 timization with PCM||0,2|C,1.2110637882,-0.9981312599,0.0309004039|C,1
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 ,-0.057420407 2|S,2.7715056244,1.1959222818,-0.2470201742|S,-2.77248357
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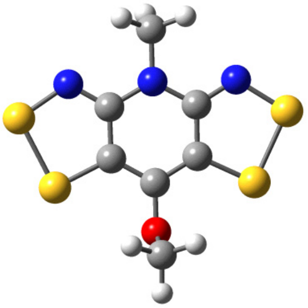

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[7] Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C. Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. W.; Morokuma, K.; Zakrzewski, V. G.; Voth, G., A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian, Inc., Wallingford CT, 2009.

2. Radical **9**, PCM based UB3LYP/6-311G(d,p) full optimization.

```
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01025987,1.6324958167,1.3980554694|O,0.3761017734,-2.7936868402,0.1493
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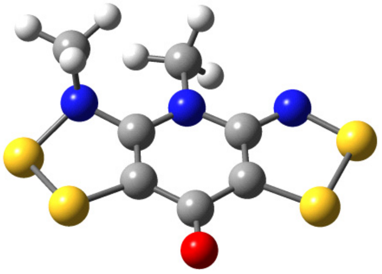

Electronic Energies (in CH_2Cl_2) of **4a** and **9**

Isomer	E(tot) Hartrees	kcal/mol	ΔH (kcal/mol)
4a (*O*-Me)	-2102.75414307	-1319477.16	0.00
9 (*N*-Me)	-2102.76193744	-1319482.06	-4.89

3. Radical **4a**, PCM UB3LYP/EPR-III/6-31G(d)//UB3LYP/6-311G(d,p) EPR properties.

```
 1|1|UNPC-RTO2008|SP|UB3LYP|GenECP|C7H6N3O1S4(2)|USER|27-Mar-2010|0||#
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al - in DCM||0,2|C,0,1.21097311,-0.99826766,0.03469571|C,0,1.197887,0.
43568511,-0.09840083|C,0,-0.00081773,1.13957615,-0.15187933|C,0,-1.198
826,0.4341859,-0.09822683|C,0,-1.2114763,-0.99981403,0.03464972|N,0,0.
00033219,-1.66741884,0.16006082|N,0,2.33247539,-1.66560723,0.04949216|
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5. Radical **9**, PCM UB3LYP/EPR-III/6-31G(d)//UB3LYP/6-311G(d,p) EPR properties.

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6. Pyridone **5a**, UB3LYP/6-311G(d,p) full optimization - Singlet State.

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 4795,-1.5348995,0.1120926,0.0001814,-0.0014826|PG=C01 [X(C6H3N3O1S4)]|
 |@
```

7. Pyridone **5a**, UB3LYP/6-311G(d,p) full optimization - Triplet State.

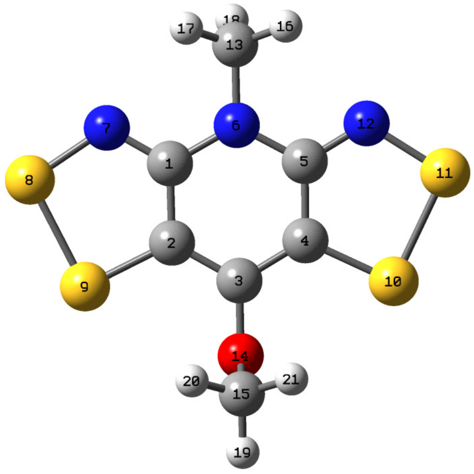
```
 1|1|UNPC-RTO-OFFICE-2008|FOpt|UB3LYP|6-311G(d,p)|C6H3N3O1S4(3)|USER|18
 -Mar-2010|0||# ub3lyp/6-311g(d,p) opt scf=tight||ub3lyp/6-311g(d,p) Tr
 iplet OBPMe - full optimization||0,3|C,-1.197612,0.755922,-0.000134|C,
 -1.20008,-0.655297,-0.000088|C,0.007397,-1.459863,0.000007|C,1.206957,
 -0.641966,-0.000025|C,1.199663,0.769523,-0.000039|N,-0.004342,1.459136
 ,-0.000414|N,-2.337012,1.442736,0.000101|S,-3.698679,0.505554,0.000223
 |S,-2.762785,-1.425406,-0.000016|S,2.771233,-1.410835,0.000081|S,3.703
 426,0.519957,0.000123|N,2.340701,1.454033,0.000128|C,-0.043923,2.92656
 4,-0.00019|O,0.015447,-2.693137,-0.000255|H,0.978157,3.29153,-0.004136
 |H,-0.574821,3.282135,-0.88429|H,-0.567878,3.282479,0.887977||Version=
 IA32W-G09RevA.02|State=3-A|HF=-2062.8283029|S2=2.024609|S2-1=0.|S2A=2.
 000318|RMSD=4.990e-009|RMSF=4.767e-005|Dipole=-0.0042854,1.1363313,-0.
 0000324|Quadrupole=7.46995,-5.6457308,-1.8242192,0.0753669,-0.0001535,
 -0.0029185|PG=C01 [X(C6H3N3O1S4)]||@
```

Section S3 EPR spectra and hyperfine coupling constants.

Radical **4a** - Calculated Properties.

Spin Densities from PCM UB3LYP/6311G(d,p) full optimization
Coupling Constants from PCM UB3LYP/EPR-III/6-31G(d)//UB3LYP/6-311G(d,p)

Number	Atom	Spin Density	Coupling Constant (Gauss)
1	C(13)	-0.070641	-6.17356
2	C(13)	0.274051	10.63731
3	C(13)	-0.144282	-9.69287
4	C(13)	0.27427	10.64685
5	C(13)	-0.070935	-6.20028
6	N(14)	-0.02295	-0.55635
7	N(14)	0.163038	2.93503
8	S(33)	0.090444	1.38891
9	S(33)	0.129653	2.50054
10	S(33)	0.130005	2.50793
11	S(33)	0.091131	1.40026
12	N(14)	0.164328	2.95936
13	C(13)	0.001275	0.12773
14	O(17)	-0.001432	1.99163
15	C(13)	-0.004279	-2.88014
16	H(1)	-0.000428	-0.27511
17	H(1)	-0.000443	-0.33645
18	H(1)	-0.001656	-0.83347
19	H(1)	-0.000366	-0.07915
20	H(1)	-0.000388	0.14424
21	H(1)	-0.000395	0.14523

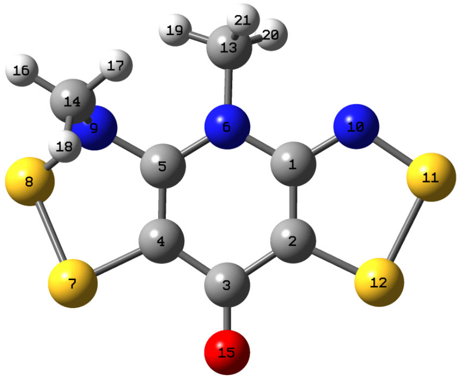


Experimental coupling constants (in Gauss) by spectral simulation:
a_N = 3.105 (2N), 0.573 (1N), a_H =0.313 (3H)
Linewidth = 0.259, g = 2.0087

Radical **9** - Calculated Properties.

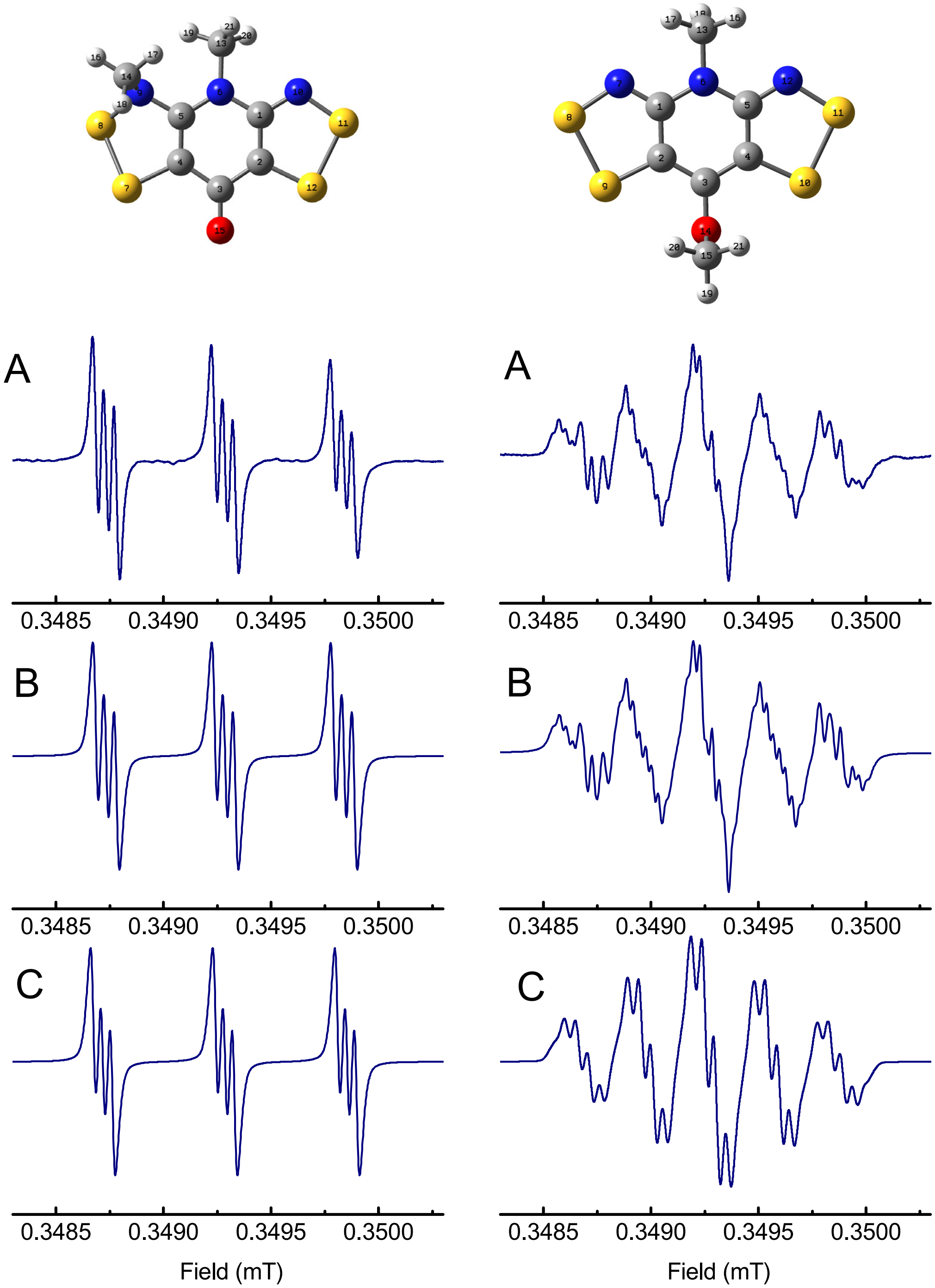
Spin Densities from PCM UB3LYP/6311G(d,p) full optimization
Coupling Constants from PCM UB3LYP/EPR-III/6-31G(d)//UB3LYP/6-311G(d,p)

Number	Atom	Spin Density	Coupling Constant (Gauss)
1	C(13)	-0.091446	-8.29091
2	C(13)	0.22603	7.25816
3	C(13)	-0.004775	-2.76328
4	C(13)	-0.010037	-1.18203
5	C(13)	0.047748	1.49652
6	N(14)	0.003815	-0.05242
7	S(33)	0.007168	0.09534
8	S(33)	-0.001655	0.16655
9	N(14)	0.001449	0.43976
10	N(14)	0.326839	5.67598
11	S(33)	0.241421	3.7714
12	S(33)	0.204241	3.98245
13	C(13)	-0.001183	-0.10388
14	C(13)	0.003412	1.55378
15	O(17)	0.046656	-0.95341
16	H(1)	0.000244	-0.03754
17	H(1)	-0.000355	-0.14006
18	H(1)	0.000119	-0.03604
19	H(1)	-0.000153	-0.04878
20	H(1)	0.000509	-0.16985
21	H(1)	-0.000047	-0.21505



Experimental coupling constants (in Gauss) by spectral simulation:
a_N = 5.526 (1N), 0.481 (1N)
Linewidth = 0.22, *g* = 2.0086

Experimental (A), simulated (B)[a,b] and calculated (C)[c] EPR spectra of **9** (left) and **4a** (right).



[a] Simulated spectrum of **4a** containg 5% of **9**.

[b] Linewidths for B and C were 0.022 mT (**9**) and 0.026 mT (**4a**).

[c] Coupling constants from PCM UB3LYP/EPR-III/6-31G(d)//UB3LYP/6-311G(d,p) calculations.