MAGNETIC RESONANCE IN CHEMISTRY, VOL. 36, 8–12 (1998)

Electrochemical and Electron Spin Resonance Investigations of Some 1,2,3-Oxa- and -Thiadiazoles

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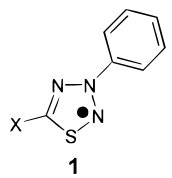
Received 14 May 1997; accepted 8 July 1997

ABSTRACT: Voltammetric studies on mesoionic 1,2,3-oxa- and -thiadiazoles confirmed that the former may be reduced irreversibly at potentials between −1.48 and −2.12 V *vs.* Fc/Fc^+ in acetonitrile at a scan rate of 200 mV s^{-1}, whereas the latter are reduced reversibly under the same conditions. The corresponding anion radicals were examined by ESR spectroscopy. Cationic alkylation products showed different electrochemical behaviour depending on the character of the heterocyclic ring. 1,2,3-Thiadiazolium ions were reduced reversibly. All coupling constants of the resulting neutral radicals were fully assigned. 1,2,3-Oxadiazolium ions were all reduced irreversibly. © 1997 John Wiley & Sons, Ltd.

KEYWORDS: ESR; oxadiazoles; thiadiazoles; cyclic voltammetry

INTRODUCTION

Radicals derived from five-membered sulphur- and nitrogen-containing rings are of current interest, owing to their (in most cases) inherent stability, making them suitable building blocks for novel conducting polymers.[1] The longevity of these radicals, on the other hand, has stimulated thorough theoretical investigations concerned mostly with calculations of spin densities.[2] The subjects of these studies were radicals from 1,2,3,5-dithiadiazoles,[3] 1,2,3,5-thiatriazoles,[4] 1,2,3-dithiazoles,[5] 1,3,2-dithiazoles[6] and 1,3,2,4-dithiadiazoles.[7] Recently, our group has reported the generation and ESR spectroscopic characterization of radicals 1 from 1,2,3,4-thiatriazoles.[8] In the course of that study, 1,2,3,4-oxatriazoles were examined in direct comparison.



1

1a: X = EtS
1b: X = EtS
1c: X = $S^{\ominus}$
1d: X = $O^{\ominus}$

We report here on our electrochemical investigation of 1,2,3-thiadiazoles (**2**) and also on our findings for 1,2,3-oxadiazoles (**4**) directly related to the 1,2,3-thiadiazoles employed.

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RESULTS AND DISCUSSION

Cyclic voltammetry

The desired radicals were to be generated by reduction of the corresponding mesoionic or cationic heterocycles. In order to obtain information on potentials and lifetimes of the radicals, cyclic voltammetry was performed on all the compounds (Table 1). Compound **2j** (sydnone) has been investigated previously in an attempt to correlate biological effects with the redox potential.[9]

The common feature of all the oxadiazoles examined is that they show only irreversible reduction at the scan rate of 200 mV s^{-1} employed. This resembles the electrochemical behaviour of 1,2- and 1,3-oxazoles, which were shown to yield ring-opened products upon electron uptake.[10]

Notable exceptions are the mesoionic 1,2,3-oxadiazoles bearing an exocyclic thiolate substituent (compounds **4g**, **h** and **i**). These show an additional reversible reduction peak in their cyclic voltammograms, indicating an electrochemically inducable rearrangement to 1,2,3-thiadiazoles comparable to that of related 1,2,3,4-oxatriazoles.[8] This behaviour is the subject of current investigations and will be reported upon elsewhere.[11] It has been exploited by us for the synthesis of **2k**. Thiadiazoles with an exocyclic olate substituent are normally prepared through ammonia-catalysed rearrangement from the isomeric oxadiazoles with an exocyclic thiolate function.[12] In the case of **2k**, this would undoubtedly have led to the amide of the carboxylic ester function present in its precursor **4h**. Therefore, we effected the rearrangement under the novel conditions of reduction of **4h** with sodium dithionite.

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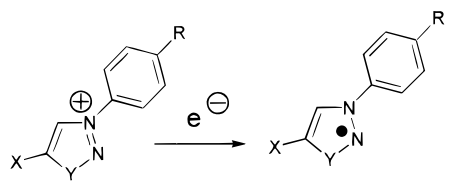
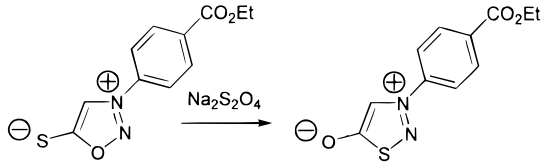


Entry	R	X	Y	Radical
2a	H	EtS	S	**3a**
2b	EtO_2C	EtS	S	**3b**
2c	MeO	EtS	S	**3c**
2d	H	EtO	S	**3d**
2e	EtO_2C	EtO	S	**3e**
2f	MeO	EtO	S	**3f**
2g	H	S-	S	**3g**
2h	EtO_2C	S-	S	**3h**
2i	MeO	S-	S	**3i**
2j	H	O-	S	**3j**
2k	EtO_2C	O^-	S	**3k**
2l	MeO	O-	S	**3l**
4a	H	EtS	O	
4b	EtO_2C	EtS	O	
4c	MeO	EtS	O	
4d	H	EtO	O	
4e	EtO_2C	EtO	O	
4f	MeO	EtO	O	
4g	H	S-	O	
4h	EtO_2C	S-	O	
4i	MeO	S-	O	
4j	H	O-	O	
4k	EtO_2C	O^-	O	

1,2,3-Thiadiazoles have not been investigated electrochemically before. In our study, all compounds were reduced reversibly at more or less negative potentials corresponding to the electronic effects the attached substituent exhibits. Compound **2f** was the only 1,2,3-thiadiazole which yielded only a very short-lived radical. This could therefore not be analysed by the technique applied.



4h **2k**

ESR investigation of the radical products

The neutral radicals **3a–3e** and anion radicals **3g–l**, generated by the reduction of substrates **2a–l** with zinc or saturated sodium dithionite solution, were identified using ESR spectroscopy (Table 2). Figure 1 shows a representative example of one of the spectra obtained. The evaluation of splitting constants of **3a–e** indicates that the structural variations in position 5 (EtS *vs.* EtO) strongly influence the *a*(N-3) value. An increase of about 0.1 mT was observed for *a*(N-3) when, without change in the *para*-phenyl substituent, EtS was replaced by EtO (compare, e.g., **3a** and **d** or **3b** and **e**). Simultaneously, higher $a(H_{ortho})$ and $a(H_{para})$ values were found in EtO-substituted radicals **3d** and **e**, whereas no significant changes occurred with the *a*(N-2) splitting constant. Owing to its small magnitude, we were able to extract the *a*(H-4) splitting only from the ESR spectra of **3d** and **e**. In other neutral radicals this value was estimated to be lower than 0.030 mT. In contrast to neutral radicals, the ESR spectra of anion radicals **3g–l** were characterized by a marked difference between the *a*(N-2) splitting of *S*-substituted radicals **3g–i** and that of *O*-substituted radicals **3j–l**, the former having about 0.1 mT higher values. As follows from the comparison of, e.g., **3g** and **j** or **3i** and **l**, the *a*(N-3) splitting remained effectively unchanged. On the other hand, enhanced *a*(H-4) values were found when proceeding from **3g–i** to **3j–l** and the same tendency was observed with the $a(H_{ortho})$ and $a(H_{para})$ splitting constants.

Table 1. Reduction potentials of cationic and mesoionic 1,2,3-oxa- and- thiadiazoles in acetonitrile vs. Fc/Fc^+ with a scan rate of 200 mV s^{-1}

Compound	Reversibility	Potential (V)	Compound	Reversibility	Potential (V)
2a	Reversible	−0.945	**4a**	Irreversible	−0.837
2b	Reversible	−0.849	**4b**	Irreversible	−0.729
2c	Reversible	−0.964	**4c**	Irreversible	−0.934
2d	Reversible	−1.096	**4d**	Irreversible	−0.979
2e	Reversible	−0.966	**4e**	Irreversible	−0.870
2f	Quasireversible	−1.160	**4f**	Irreversible	−1.140
2g	Reversible	−1.595	**4g**	Irreversible	−1.564
				Reversible	−1.919
2h	Reversible	−1.440	**4h**	Irreversible	−1.477
				Reversible	−1.725
2i	Reversible	−1.645	**4i**	Irreversible	−1.668
				Reversible	−1.968
2j	Reversible	−1.915	**4j**	Irreversible	−2.014
2k	Reversible	−1.710	**4k**	Irreversible	−1.819
2l	Reversible	−1.899	**4l**	Irreversible	−2.119

Table 2. Isotropic hyperfine coupling constants (mT) of neutral and anionic 1,2,3-thiadiazolyls **3** in toluene or CH_2Cl_2

Radical	*a*(N-2)	*a*(N-3)	*a*(H-4)	*a*(H-2′,6′)	*a*(H-4′)	*a*(H-3′5′)
3a	0.987	0.344	—	0.109	0.109	0.039
3b	0.984	0.285	—	0.110	—	0.039
3c	0.987	0.364	—	0.105	—	—
3d	0.950	0.450	0.046	0.148	0.168	0.059
3e	0.940	0.360	0.085	0.150	—	0.046
3f	—	—	—	—	—	—
3g	0.881	0.380	0.114	0.162	0.171	0.053
3g (calc.)	0.952	0.226	0.215	0.200	0.268	0.056
3g · H† (calc.)	1.089	0.352	0.005	0.151	0.168	0.055
3h	0.880	0.379	0.120	0.162	—	0.054
3i	0.877	0.443	0.104	0.156	—	0.053
3j	0.776	0.380	0.180	0.199 (1H) 0.218 (1H)	0.238	0.052
3k	0.766	0.383	0.175	0.195 (1H) 0.211 (1H)	—	0.055
3l	0.771	0.447	0.175	0.200	—	0.062
1a	1.051	0.578	0.027	0.150	0.150	0.048
1b	1.045	0.674	0.020	0.164	0.164	0.054
1c	0.950	0.531	0.055	0.170	0.190	0.055
1d	0.891	0.534	0.102	0.216	0.211	0.058

The above-mentioned substitution effects satisfactorily correlate with those in the previously studied neutral and anion radicals **1** from 1,2,3,4-thiatriazoles.

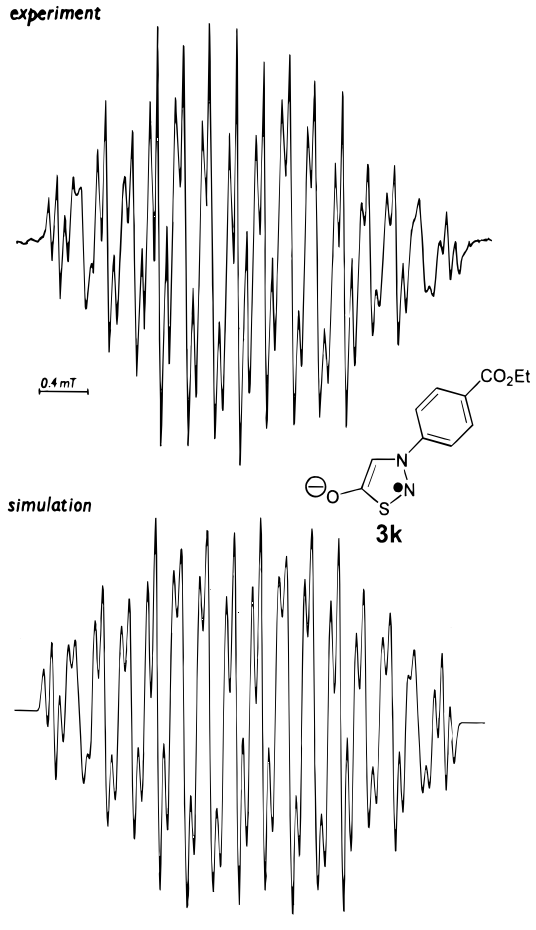


Figure 1. ESR spectrum (top) of radical **3k** generated by electrochemical reduction of a 2 mM solution of **2k** in DMF (0.1 M n-Bu_4NBF_4) and its simulation (bottom).

The ESR data for **1a–d** (Table 2), when compared with the splitting constants of **3a**, **d**, **g** and **j**, suggest that the same replacement in position 5 (EtS *vs.* EtO or S^- *vs.* O^-) gives rise to a similar spin density redistribution in both heterocyclic rings. Based on the similarity of the 1,2,3-thiadiazole and 1,2,3,4-thiatriazole rings, the assignment of two nitrogen splitting constants to positions 2 and 3 in **3a–l** was carried out without using ^{15}N-labelled substances **1** [*a*(N-2) > *a*(N-3)].

Density functional theory (DFT) calculations were performed for **3g** and for protonated **3g**, **3g** · H^+. The geometry of the two radicals was optimized by means of 3–21G. All single-point calculations were made by 6–31G*. As a result, **3g** and **3g** · H^+ were calculated to be planar, or nearly planar. The calculated and measured coupling constants matched fairly well. This can be regarded as proof of the cyclic nature of radicals **3**. Open-chain structures have been ruled out for the closely related radicals **1** by similar arguments.[8]

Comparison of the calculated coupling constants for the non-protonated and the protonated radical anion shows that they differ only for proton H-4. Unfortunately, in the case of this proton, the calculated values of *a*(H-4) are equally far from the measured value. As in the case of radicals **1**,[8] we tend to the conclusion that the anion radicals in this study are protonated.

EXPERIMENTAL

ESR spectra were recorded using an ERS-300 X-band spectrometer (ZWG, Berlin, Germany) using a 100 kHz field modulation, a microwave frequency of 9.2 GHz and a magnetic field strength of 330 mT. Cyclic voltammetry (CV) was performed either with an ECM 700 (ZWG) or a Princeton Applied Research Model 270 instrument (EG&G PAR, Princeton, NJ, USA) in ace-

tonitrile which was 0.1 M in tetrabutylammonium tetrafluoroborate *vs.* Ag/AgCl. NMR spectra were measured with a Bruker AC 200 T system. Solvents and supporting electrolytes were of electrochemical grade, purchased from Fluka (Buchs, Switzerland) and used without further purification. For ESR spectra using electrochemical reduction, dichloromethane was the solvent. For CV and ESR, the concentration of the compounds was *ca.* 1 mM. All solutions were thoroughly purged with nitrogen prior to use. All compounds refused to be reversibly oxidised up to +1.5 V. In this context, the term reversible applies to scan rates between 0.05 and 1 V s^{-1}.

Compounds

The following compounds have been described previously: **2d**,[12] **2g**,[12] **2j**,[12] **4d**,[12] **4g**,[12] **4j**,[13] **4k**[14] and **4l**.[13]

Ethylations of mesoionic compounds **2g–l** and **4g–l** to yield cations **2a–c**, **e**, **f**, **h** and **i** and **4a–c**, **e** and **f** were performed with triethyloxonium tetrafluoroborate following the published procedure.[12]

2a. 79%; m.p. 59–60 °C. Found: C, 38.86; H, 3.58; N, 9.04; S, 20.80. $C_{10}H_{11}BF_4N_2S_2$ requires C, 38.73, H, 3.57; N, 9.03, S, 20.68%. ^{1}H NMR ($CDCl_3$): 1.42 ppm (3H, t, *J* 7.38 Hz, CH_3), 3.35 ppm (2H, q, *J* 7.38 Hz, CH_2), 7.44–7.66 ppm (3H, m, 3-, 4-, 5-H in Ph), 7.96–8.02 ppm (2H, m, 2-, 6-H in Ph), 9.55 ppm (1H, s, 4-H). ^{13}C NMR ($CDCl_3$): 13.08 (CH_3), 31.46 (CH_2), 122.66 (3-, 5-C in Ph), 130.44 (2-, 6-C in Ph), 133.20 (4-C in Ph), 138.44 (4-C), 139.31 (1-C in Ph), 169.55 ppm (5-C).

2b. 96%; m.p. 95–96 °C. Found: C, 40.93; H, 3.93; N, 7.38; S, 16.77. $C_{13}H_{15}BF_4N_2O_2S_2$ requires C, 40.85, H, 3.96; N, 7.33, S, 16.78%. ^{1}H NMR (acetone-d_6–TFA, 100:1): 1.40 ppm (3H, t, *J* 7.03 Hz, CH_3 in ester), 1.55 ppm (3H, t, *J* 7.39 Hz, CH_3), 3.61 ppm (2H, q, *J* 7.39 Hz, CH_2), 4.43 ppm (2H, q, *J* 7.03 Hz, CH_2 in ester), 8.32–8.37 ppm (4H, m, 2-, 3-, 5-, 6-H in Ph), 10.21 ppm (1H, s, 4-H). ^{13}C NMR (acetone-d_6–TFA, 100:1): 13.67 (CH_3), 14.38 (CH_3 in ester), 31.87 (CH_2), 62.50 (CH_2 in ester), 124.36 (2-, 6-C), 132.20 (3-, 5-C), 135.43 (4-C in Ph), 141.23 (4-C), 143.42 (1-C), 165.25 (C=O), 170.14 ppm (5-C).

2c. 81%; m.p. 81–82 °C. Found: C, 38.89; H, 3.79; N, 8.21; S, 18.57. $C_{11}H_{13}BF_4N_2OS_2$ requires C, 38.84, H, 3.85; N, 8.24, S, 18.85%. ^{1}H NMR (acetone-d_6–TFA, 100:1): 1.53 ppm (3H, t, *J* 7.30 Hz, CH_3), 3.57 ppm (3H, q, *J* 7.30 Hz, CH_2), 3.96 ppm (3H, s, OCH_3), 7.25–7.28 ppm (2H, m, 3-, 5-H in Ph), 8.11–8.14 ppm (2H, m, 2-, 6-H in Ph), 10.00 ppm (1H, s, 4-H). ^{13}C NMR (acetone-d_6–TFA, 100:1): 13.69 (CH_3), 31.75 (CH_2), 56.54 (OCH_3), 116.27 (3-, 5-C in Ph), 125.49 (2-, 6-C in Ph), 134.11 (1-C in Ph), 139.91 (4-C), 164.23 (4-C in Ph), 169.13 ppm (5-C).

2e. 85%; m.p. 125–126 °C. Found: C, 42.46; H, 4.06; N, 7.61; S, 8.60. $C_{13}H_{15}BF_4N_2O_3S$ requires C, 42.64; H, 4.13; N, 7.65; S, 8.76%. ^{1}H NMR (acetone-d_6–TFA, 100:1): 1.41 ppm (3H, t, *J* 7.13 Hz, CH_3 in ester), 1.61 ppm (3H, t, *J* 7.06 Hz, CH_3), 4.43 ppm (2H, q, *J* 7.13 Hz, CH_2 in ester), 4.84 ppm (2H, q, *J* 7.06 Hz, CH_2), 8.31–8.36 ppm (4H, m, 2-, 3-, 5-, 6-H in Ph), 10.03 ppm (1H, s, 4-H). ^{13}C NMR (acetone-d_6–TFA, 100:1): 14.38 (CH_3 in ester), 14.74 (CH_3), 62.45 (CH_2 in ester), 77.47 (CH_2), 123.90 (2-, 6-C), 129.15 (4-C), 132.10 (3-, 5-C), 135.00 (4-C in Ph), 143.91 (1-C), 165.21 (C=O), 184.92 ppm (5-C).

2f. 65%; m.p. 142–143 °C. Found: C, 41.02; H, 4.23; N, 8.69; S, 9.80. $C_{11}H_{13}BF_4N_2O_2S$ requires C, 40.76; H, 4.04, N, 8.64; S, 9.89%. ^{1}H NMR (acetone-d_6–TFA, 100:1): 1.61 ppm (3H, t, *J* 6.95 Hz, CH_3), 4.00 ppm (3H, s, OCH_3), 4.82 ppm (3H, q, *J* 6.95 Hz, CH_2), 7.26–7.29 ppm (2H, m, 3-, 5-H in Ph), 8.11–8.14 ppm (2H, m, 2-, 6-H in Ph), 9.87 ppm (1H, s, 4-H). ^{13}C NMR (acetone-d_6–TFA, 100:1): 14.51 (CH_3), 56.54 (OCH_3), 77.27 (CH_2), 116.23 (3-, 5-C), 125.07 (2-, 6-C), 127.94 (4-C), 134.81 (1-C in Ph), 164.20 (4-C in Ph), 184.44 ppm (5-C).

4a. 71%; m.p. 79–80 °C. Found: C, 40.82; H, 3.79; N, 9.36; S, 10.81. $C_{10}H_{11}BF_4N_2OS$ requires C, 40.84 H, 3.77; N, 9.53, S, 10.90%. ^{1}H NMR (acetone-d_6–TFA, 100:1): 1.59 ppm (3H, t, *J* 7.32 Hz, CH_3), 3.67 ppm (2H, q, *J* 7.32 Hz, CH_2), 7.84–7.98 ppm (3H, m, 3-, 4-, 5-H in Ph), 8.20–8.24 ppm (2H, m, 2-, 6-H in Ph), 9.62 ppm (1H, s, 4-H). ^{13}C NMR (acetone-d_6–TFA, 100:1): 14.92 (CH_3), 29.06 (CH_2), 122.51 (4-C), 124.01 (3-, 5-C in Ph), 131.77 (2-, 6-C in Ph), 133.74 (1-C in Ph), 135.55 (4-C in Ph), 178.48 ppm (5-C).

4b. 93%; m.p. 111–112 °C. Found: C, 42.50; H, 4.18; N, 7.58; S, 8.48. $C_{13}H_{15}BF_4N_2O_3S$ requires C, 42.64; H, 4.13, N, 7.65; S, 8.76%. ^{1}H NMR (acetone-d_6–TFA, 100:1): 1.41 ppm (3H, t, *J* 7.09 Hz, CH_3 in ester), 1.59 ppm (3H, t, *J* 7.28 Hz, CH_3), 3.67 ppm (2H, q, *J* 7.28 Hz, CH_2), 4.44 ppm (2H, q, *J* 7.09 Hz, CH_2 in ester), 8.32–8.44 ppm (4H, m, 2-, 3-, 5-, 6-H in Ph), 9.71 ppm (1H, s, 4-H). ^{13}C NMR (acetone-d_6–TFA, 100:1): 14.40 (CH_3 in ester), 14.87 (CH_3), 29.50 (CH_2), 62.64 (CH_2 in ester), 122.86 (4-C), 124.51 (2-, 6-C), 132.45 (3-, 5-C), 136.53 (4-C in Ph), 136.88 (1-C), 165.00 (C=O), 179.01 ppm (5-C).

4c. 78%; m.p. 121–122 °C. Found: C, 40.83; H, 4.06; N, 8.59; S, 9.78. $C_{11}H_{13}BF_4N_2O_2S$ requires C, 40.76; H, 4.04, N, 8.64; S, 9.89%. ^{1}H NMR (acetone-d_6–TFA, 100:1): 1.58 ppm (3H, t, *J* 7.44 Hz, CH_3),3.64 ppm (2H, q, *J* 7.44 Hz, CH_2), 3.99 ppm (3H, s, OCH_3), 7.34–7.37 ppm (2H, m, 3-, 5-H in Ph), 8.14–8.17 ppm (2H, m, 2-, 6-H in Ph), 9.58 ppm (1H, s, 4-H). ^{13}C NMR (acetone-d_6–TFA, 100:1): 14.96 (CH_3), 29.29 (CH_2), 56.73 (OCH_3), 116.92 (3-, 5-C), 121.69 (4-C), 125.61 (2-, 6-C), 126.27 (1-C in Ph), 165.57 (4-C in Ph), 177.84 ppm (5-C).

4e. 82%; m.p. 104–105 °C. Found: C, 44.80; H, 4.33; N, 7.99. $C_{13}H_{15}BF_4N_2O_4$ requires C, 44.60; H, 4.32; N, 8.00%. ^{1}H NMR ($CDCl_3$): 1.43 ppm (3H, t, *J* 7.09 Hz, CH_3 in ester), 1.56 ppm (3H, t, *J* 7.04 Hz, CH_3), 4.44 ppm (2H, q, *J* 7.09 Hz, CH_2 in ester), 4.87 ppm (2H, q, *J* 7.04 Hz, CH_2), 8.11 ppm (2H, d, *J* 8.81 Hz, 3-, 5-H), 8.27 ppm (2H, d, *J* 8.81 Hz, 2-, 6-H), 8.89 ppm (1H, s, 4-H). ^{13}C NMR ($CDCl_3$): 14.18 (2 CH_3), 62.16 (CH_2 in ester), 76.61 (CH_2),103.41 (4-C), 122.59 (2-, 6-C), 131.77 (3-, 5-C), 135.68 (4-C in Ph), 135.98 (1-C), 164.13 (C=O), 173.71 ppm (5-C).

4f. 83%; m.p. 114–115 °C. Found: C, 42.45; H, 4.19; N, 8.97. $C_{11}H_{13}BF_4N_2O_3$ requires C, 42.89; H, 4.25; N, 9.09%. ^{1}H NMR (acetone-d_6–TFA, 100:1): 1.63 ppm (3H, t, *J* 7.04 Hz, CH_3), 4.00 ppm (3H, s, OCH_3), 5.00 ppm (2H, q, *J* 7.04 Hz, CH_2), 7.30–7.38 ppm (2H, m, 3-, 5-H), 8.09-8.16 ppm (2H, m, 2-, 6-H), 9.04 ppm (1H, s, 4-H). ^{13}C NMR (acetone-d_6–TFA, 100:1): 14.39 (CH_3), 56.68 (OCH_3), 76.51 (CH_2), 104.04 (4-C), 116.69 (3-, 5-C), 125.12 (2-, 6-C), 126.89 (1-C in Ph), 165.23 (4-C in Ph), 174.36 ppm (5-C).

Mesoions with exocyclic thiolate functions, **2h** and **i**, were prepared by thiolation of the corresponding mesoions with exocyclic olate groups, **2k** and **l**, with Lawesson's reagent,[15] as follows.

2h. 79%; m.p. 163–165 °C. Found: C, 49.37; H, 3.70; N, 10.53; S, 24.10. $C_{11}H_{10}N_2O_2S_2$ requires C, 49.60; H, 3.78; N, 10.52; S, 24.08%. ^{1}H NMR ($CDCl_3$): 1.36 ppm (3H, t, *J* 7.14 Hz, CH_3), 4.37 ppm (2H, q, *J* 7.14 Hz, CH_2), 7.78–7.82 ppm (2H, m, 3-, 5-H), 8.19–8.24 ppm (2H, m, 2-, 6-H), 8.47 ppm (1H, s, 4-H). ^{13}C NMR ($CDCl_3$): 14.23 (CH_3), 61.91 (CH_2), 121.80 (3-, 5-C), 131.57 (2-, 6-C); 133.82 (4-C in Ph), 139.38 (4-C), 142.08 (1-C), 164.58 (C=O), 191.13 ppm (5-C).

2i. 69%; m.p. 166–168 °C. Found: C, 47.94; H, 3.62; N, 12.45; S, 28.34. $C_9H_8N_2OS_2$ requires C, 48.19; H, 3.60; N, 12.49; S, 28.59%. ^{1}H NMR ($CDCl_3$): 3.82 ppm (3H, s, CH_3), 6.96–7.01 ppm (2H, m, 3-, 5-H), 7.61–7.66 ppm (2H, m, 2-, 6-H), 8.38 ppm (1H, s, 4-H). ^{13}C NMR ($CDCl_3$): 55.81 (CH_3), 115.08 (3-, 5-C), 123.10 (2-, 6-C); 132.76 (1-C in Ph), 138.85 (4-C), 162.12 (4-C in Ph), 190.15 ppm (5-C).

Mesoions **4h** and **i** were prepared from cations **4e** and **f** by the method described previously for the synthesis of **2j**.[12] An ethanolic solution of NaSH was freshly prepared from Na_2S and $NaHCO_3$ in water by precipitating Na_2CO_3 with ethanol.

4h. 69%; m.p. 133–134 °C. Found: C, 53.42; H, 4.21; N, 10.89; S, 12.43. $C_{11}H_{10}N_2O_3S$ requires C, 52.79;
H, 4.03; N, 11.19; S, 12.81%. ^{1}H NMR ($CDCl_3$): 1.41 ppm (3H, t, *J* 7.12 Hz, CH_3), 4.42 ppm (2H, q, *J* 7.12 Hz, CH_2), 7.72 ppm (1H, s, 4-H), 7.86 ppm (2H, d, *J* 8.84 Hz, 3-, 5-H in Ph), 8.30 ppm (2H, d, *J* 8.84 Hz, 2-, 6-H). ^{13}C NMR ($CDCl_3$): 14.17 (CH_3), 62.01 (CH_2), 116.68 (4-C), 121.59 (3-, 5-C in Ph), 131.74 (2-, 6-C in Ph), 134.83 (4-C in Ph), 135.94 (1-C in Ph), 164.31 (C=O), 190.58 ppm (5-C).

4i. 80%; m.p. 186–187 °C. Found: C, 51.68; H, 3.89; N, 13.45; S, 15.32. $C_9H_8N_2O_2S$ requires C, 51.91; H, 3.87; N, 13.45; S, 15.40%. ^{1}H NMR ($CDCl_3$): 3.91 ppm (3H, s, CH_3), 7.07–7.12 ppm (2H, m, 3-, 5-H), 7.44 ppm (1H, s, 4-H), 7.63–7.68 ppm (2H, m, 2-, 6-H in Ph). ^{13}C NMR ($CDCl_3$): 55.95 (CH_3), 115.62 (3-, 5-C in Ph), 116.15 (4-C), 122.99 (2-, 6-C), 163.09 (4-C), 163.09 (1-C in Ph), 190.45 ppm (5-C).

Compound **2k** was prepared from **4h** in the following way. To a yellow solution of 1 mmol of **4h** in 40 ml of boiling ethanol was added 1 g of sodium dithionite in 10 ml of water under argon over a period of 1 h. Stirring was continued for 30 min. The ethanol was removed under vacuum and the remaining colourless residue was taken up in CH_2Cl_2, extracted twice with water, dried and evaporated. Recrystallization from ethanol–CH_2Cl_2 gave 113 mg (45%) of **2k** as needles, m.p. 155–156 °C. Found: C, 52.76; H, 3.98; N, 11.29; S, 12.84. $C_{11}H_{10}N_2O_3S$ requires C, 52.79; H, 4.03; N, 11.19; S, 12.81%. ^{1}H NMR ($CDCl_3$): 1.36 ppm (3H, t, *J* 7.20 Hz, CH_3), 4.37 ppm (2H, q, *J* 7.20 Hz, CH_2), 7.76–7.80 ppm (2H, m, 3-, 5-H in Ph), 7.89 ppm (1H, s, 4-H), 8.16–8.21 ppm (2H, m, 2-, 6-H in Ph). ^{13}C NMR ($CDCl_3$): 14.24 (CH_3), 61.77 (CH_2), 120.46 (4-C), 121.59 (3-, 5-C), 131.29 (2-, 6-C), 133.36 (4-C in Ph), 143.60 (1-C), 164.79 (C=O), 185.62 ppm (5-C).

Compound **2l** was prepared from **4i** by the ammonia-catalysed rearrangement described for **2j**:[12] 87%; m.p. 169–170 °C. Found: C, 51.72; H, 3.81; N, 13.42; S, 15.15. $C_9H_8N_2O_2S$ requires C, 51.91; H, 3.87; N, 13.45; S, 15.40%. ^{1}H NMR ($CDCl_3$): 3.91 ppm (3H, s, CH_3), 7.05–7.08 ppm (2H, m, 3-, 5-H in Ph), 7.83 (1H, s, 4-H), 7.69–7.71 ppm (2H, m, 2-, 6-H in Ph). ^{13}C NMR ($CDCl_3$): 56.21 (CH_3), 120.55 (4-C), 115.28 (3-, 5-C), 123.36 (2-, 6-C), 134.84 (1-C in Ph), 162.11 (4-C), 186.39 ppm (5-C).

Acknowledgements

We are very grateful to D. Sperling for the performance of the *ab initio* calculations. Valuable technical assistance was provided by Mrs B. Schandert and Mrs U. Feist.

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