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# Phosphorus, Sulfur, and Silicon and the Related Elements

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EPR Spectra and Spin Density Distribution of O,S-Dimethyl 4,4-Dithioterephthalate Radical Anions

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### EPR SPECTRA AND SPIN DENSITY DISTRIBUTION OF *O*,*S*-DIMETHYL 4,4-DITHIOTEREPHTHALATE RADICAL ANIONS

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#### **GRAPHICAL ABSTRACT**



**Abstract** The preparation of O-methyl S-trideuteromethyl 4,4-dithioterephthalate and Smethyl O-trideuteromethyl 4,4-dithioterephthalate is described. The EPR spectra of the corresponding radical anions are measured. Comparison with the spectrum of O,S-dimethyl 4,4dithioterephthalate radical anions allows the unequivocal assignment of the proton hyperfine structure (proton "hfs") coupling constants in the above asymmetric species. Assignment of the arene proton hfs coupling constants is achieved by PM6 and density functional theory MO calculations of the spin density distribution and application of McConnell's relationship  $a_{\mu}^{\rm H} =$  $-2.4 \cdot \rho^{\pi}{}_{\mu}$ . The spin density distribution in the asymmetric title compound is compared with those in the radical anions of dimethyl terephthalate and the corresponding symmetric sulfur analogs.

**Keywords** Trideuteromethanethiol; dimethyl 4,4-dithioterephthalates; in-situ electroreduction; radical anions; electron paramagnetic resonance (EPR) spectroscopy; molecular orbital (MO) calculations

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#### INTRODUCTION

We have comprehensively studied the influence of electron-withdrawing substituents such as thiolo (CO-SR), thiono (CS-OR), and dithiocarboxylate (CS-SR) groups on the spin density distribution  $\rho_{\mu}^{\pi}$  in the radical anions<sup>1</sup> of aromatic  $\pi$ -electron systems, for example, in the benzene,<sup>2</sup> naphthalene,<sup>3</sup> and the nonalternating azulene<sup>4</sup> series. The effect of one single or two identical electron-withdrawing groups on  $\rho_{\mu}^{\pi}$  can be determined rather easily via EPR spectroscopic measurements of the proton hyperfine structure (proton "hfs") coupling constants  $a_{\mu}^{\rm H}$  and application of the McConnell relationship  $a_{\mu}^{\rm H} = \mathbf{Q} \cdot \rho_{\mu}^{\pi}$ . The necessary assignment of  $a_{\mu}^{\rm H}$  to a specific center  $\mu$  is unequivocal in most of these cases.

The interaction of two different electron-withdrawing substituents with an aromatic  $\pi$ -electron system, on the other hand, is more difficult to explore because the assignment of the hfs coupling constants is not as straightforward. Since we were, however, particularly interested in the competition between substituents such as CO-OR and CS-SR, we have performed further experiments and MO theoretical calculations on the radical anions of dimethyl terephthalate (6) and its various sulfur analogs 3 and 7–10, and thus present our results here. In order to unequivocally assign the methyl proton hfs coupling constants of the asymmetric radical anion 3<sup>•-</sup>, we synthesized its deuterium-labeled derivatives 4 and 5 and recorded the EPR spectra of their in-situ electro-generated radical anions. In addition, we performed new MO calculations by the use of modern semi-empirical and density functional theory (DFT) methods in order to get a better understanding of the complex spin density distribution in the bifunctional radical anions 3<sup>•-</sup> to 10<sup>•-</sup> and its dependence on the torsion angle  $\Theta$  between the plane of the benzene ring and the planar functional groups.

#### **RESULTS AND DISCUSSION**

We prepared the desired *O*-trideuteromethyl dithioester **4** from 4-cyanobenzoyl chloride via trideuteromethyl 4-cyanobenzoate (**2**), and the *S*-trideuteromethyl dithioester **5** from methyl 4-cyanobenzoate (**1**) according to known procedures for the preparation of **3**. Trideuteromethanethiol that was required for the preparation of **5** was prepared from trideuteroiodomethane via *S*-trideuteromethylisothiouronium iodide.



The three dithioesters **3**, **4**, and **5** were transformed into persistent radical anions by in-situ electroreduction in dry dimethyl sulfoxide (DMSO) in the cavity of the EPR spectrometer as described earlier.<sup>2b,5</sup> The observed EPR spectra are shown in Figures 1–3.

They exhibit a better resolution and a higher signal-to-noise ratio as compared with our earlier results.<sup>2b</sup> The proton hfs coupling constants could, therefore, be determined from the spectra more precisely. They were verified by simulation and are compiled in Table 1.

$a_{2,6}^{\rm H}$	$a_{3,5}^{\rm H}$	$a_{\rm OMe}^{\rm H}$	$a_{\mathrm{SMe}}^{\mathrm{H}}$	g-factor
0.046	0.300	0.046	0.127	2.00790
0.058	0.287	0.007 <sup>a</sup>	0.123	2.00793
0.052	0.279	0.052	0.021 <sup>a</sup>	2.00788
	<i>a</i> <sup>H</sup> <sub>2,6</sub> 0.046 0.058 0.052	$\begin{array}{c} a_{2,6}^{\rm H} & a_{3,5}^{\rm H} \\ \hline 0.046 & 0.300 \\ 0.058 & 0.287 \\ 0.052 & 0.279 \end{array}$	$a_{2,6}^{\rm H}$ $a_{3,5}^{\rm H}$ $a_{\rm OMe}^{\rm H}$ 0.0460.3000.0460.0580.2870.007^a0.0520.2790.052	$a_{2,6}^{\rm H}$ $a_{3,5}^{\rm H}$ $a_{\rm OMe}^{\rm H}$ $a_{\rm SMe}^{\rm H}$ 0.0460.3000.0460.1270.0580.2870.007^a0.1230.0520.2790.0520.021^a

**Table 1** Proton hfs coupling constants  $a^{\rm H}_{\mu}$  (mT) and *g*-factors of **3**<sup>•-</sup> to **5**<sup>•-</sup>

 $^{a}Me = CD_{3}.$ 







Figure 2 Experimental (left) and simulated (right) EPR spectrum of 4<sup>•-</sup>.



Figure 3 Experimental (left) and simulated (right) EPR spectrum of 5<sup>•-</sup>.

The largest observed coupling constant turned out to be  $a^{\text{H}} = 0.300 \text{ mT}$  rather than the previously reported<sup>2b</sup> value 0.238 mT.

It is obvious from the data that the splitting of 0.127 mT in  $3^{\bullet-}$  is due to the *S*-methyl protons since it nearly disappears in  $5^{\bullet-}$ . Simulation with  $a_{SCD3}^D = 0.020$  mT (0.127:6.5) and  $a_{OCH3}^H = a_{2,6}^H = 0.052$  mT results in the EPR spectrum of  $5^{\bullet-}$  consisting of only three resolved broad lines due to  $a_{3,5}^H = 0.279$  mT as shown in Figure 3. The smaller splitting of 0.046 mT in the spectrum of  $3^{\bullet-}$  thus belongs to the *O*-methyl protons. Accordingly, it is missing in the spectrum of  $4^{\bullet-}$ . This result,  $a_{SMe}^H > a_{OMe}^H$ , is not unexpected. It corresponds with the observed coupling constants  $a_{SMe}^H = 0.108$  mT in dimethyl tetrathioterephthalate  $9^{\bullet-}$  versus  $a_{OMe}^H = 0.078$  mT in dimethyl terephthalate radical anions  $6^{\bullet-}$  <sup>2b</sup> and is also observed for the pair methyl dithiobenzoate ( $a_{SMe}^H = 0.108$  mT)<sup>2a</sup> and methyl benzoate ( $a_{OMe}^H = 0.094$  mT).<sup>6</sup>

The assignment of the coupling constants of the aromatic protons to the 2,6- or the 3,5positions of  $3^{\bullet-}$  to  $5^{\bullet-}$  was not quite as straightforward. An experimental assignment was not possible since the dithioester with specifically deuterium labeled arene ring positions was not at our disposal. The corresponding coupling constants could, however, be calculated from the spin densities by use of the McConnell relationship  $a^{\rm H}_{\mu} = \mathbf{Q} \cdot \rho^{\pi}_{\mu}$  (as discussed later).

We could measure the g-factors  $(2.00790 \pm 0.00003)$  of the three radical anions  $3^{\bullet-}$ ,  $4^{\bullet-}$ , and  $5^{\bullet-}$  (see the Table) more precisely as previously.<sup>2b</sup> They agree with each other within the limits of experimental error (see Table 1). The high value is due to the spin orbit-coupling (heavy-atom effect) of the thiocarbonyl sulfur atom. This effect is even more pronounced for the dimethyl tetrathioterephthalate radical anion  $9^{\bullet-}$  with g = 2.0095.<sup>2b</sup> It is, in a semiquantitative sense, indicative of a high spin density  $\rho^{\pi}$  in the dithioester substituent,<sup>2a,3</sup> although a correct calculation of  $\rho^{\pi}$  from g is not easily possible since the electron excitation energy  $\Delta E(n \rightarrow \pi^*)$  and the symmetry of the g-tensor are not known in the present case.

#### **MO CALCULATIONS**

In order to achieve a better understanding of the spin density distribution and to be able to assign the hfs coupling constants of the arene protons by use of McConnell's relationship  $a^{\rm H}_{\mu} = -2.4 \cdot \rho^{\pi}_{\mu}$ , we performed semiempirical PM6 type and DFT MO calculations<sup>7</sup> on **3**<sup>•-</sup>. In addition, we included the results of new PM6-MO calculations on the spin density distribution in the related radical anions **6**<sup>•-</sup> to **10**<sup>•-</sup>. The results are compiled in Table 2.



The PM6 results obtained for  $3^{\bullet-}$  do not deviate much from the more sophisticated ab-initio-DFT [B3Lyp1 ROHF 6–31G (p,d)] values. We have, therefore, only used PM6 calculations for  $6^{\bullet-}$  to  $10^{\bullet-}$  because of the much longer calculation times required for DFT calculations.

Although the quantitative agreement with the experimental data for  $3^{\bullet-}$  is not excellent, the assignment of the larger, average coupling constant  $a_{3,5}^{\rm H} = 0.289$  mT to the arene protons 3-H and 5-H neighboring the CS-SMe group and of the smaller one  $a_{2,6}^{\rm H} = 0.052$  mT to the protons 2-H and 6-H neighboring the CO-OMe group is unequivocal.

Not unexpectedly, the spin density within the dithioester radical anions  $3^{\bullet-}$  and the thionoester radical anions  $7^{\bullet-}$  is shifted toward the thiocarbonyl group. This effect is

Comp.		$\rho_1^{\pi}$	$\rho_2^{\pi}$	$\rho_3^{\pi}$	$ ho_4^{\pi}$	$\rho_5^{\pi}$	$ ho_6^{\pi}$	$\rho^{\pi}_{\rm C(O)}$	$ ho_{\mathrm{O}}^{\pi}$	$\rho^{\pi}_{\rm C(S)}$	$\rho_{\rm S}^{\pi}$
3•-	Exp <sup>a</sup>	_	0.022	0.120		0.120	0.022	_		_	
	PM6	0.115	0.033	0.069	0.091	0.076	0.024	0.024	0.019	0.230	0.254
	DFT	0.104	0.021	0.067	0.068	0.061	0.027	0.043	0.042	0.241	0.261
6•-	Exp <sup><i>a,b</i></sup>	_	0.065	0.065	_	0.065	0.065	_	_	_	_
	PM6	0.207	0.076	0.076	0.207	0.077	0.077	0.074	0.050	_	_
<b>7</b> ∙−	Exp <sup><i>a,b</i></sup>	_	0.021	0.110	_	0.110	0.021	_	_	_	_
	PM6	0.165	0.051	0.088	0.135	0.085	0.040	0.041	0.031	0.179	0.130
<b>8</b> •−	Exp <sup><i>a,b</i></sup>	_	0.050	0.050	_	0.050	0.050	_	_	_	_
	PM6	0.133	0.068	0.056	0.133	0.068	0.056	_	_	0.117	0.094
9•-	Exp <sup><i>a,b</i></sup>	_	0.045	0.045	_	0.045	0.045	_	_	_	_
	PM6	0.097	0.055	0.045	0.097	0.045	0.055	_	_	0.122	0.148
10•-	$Exp^{a,b}$	_	0.056	0.056	_	0.056	0.056	_	_	_	_
	PM6	0.180	0.071	0.075	0.180	0.071	0.075	0.093	0.066 <sup>c</sup>	_	_

**Table 2** Spin densities  $\rho_{\mu}^{\pi}$  in the radical anions  $3^{\bullet-}$  and  $6^{\bullet-}$  to  $10^{\bullet-}$ 

 ${}^a \rho^{\pi}{}_{\mu} = a^{\rm H}_{\mu}$  / –2.4; average values of  $a^{\rm H}_{\mu}$  from  $\mathbf{3}^{\bullet-}$ ,  $\mathbf{4}^{\bullet-}$ , and  $\mathbf{5}^{\bullet-}$  were used.

<sup>&</sup>lt;sup>b</sup>From Ref. 2b.

 $<sup>^{</sup>c}\rho^{\pi}s.$ 



Figure 4 Calculated (PM6) spin density distribution in 3<sup>•-</sup>.

not only reflected in the hfs coupling constants of the arene protons but is also evident from the calculated values  $\rho^{C}_{CS} = 0.241 (3^{\bullet-})/0.179 (7^{\bullet-})$  and  $\rho^{S}_{CS} = 0.261 (3^{\bullet-})/0.130$  $(7^{\bullet-})$  compared with  $\rho^{C}_{CO} = 0.043 (3^{\bullet-})/0.041 (7^{\bullet-})$  and  $\rho^{\circ}_{CO} = 0.042 (3^{\bullet-})/0.031 (7^{\bullet-})$  (see Table 2). Unfortunately, we could not experimentally prove this result, which is also demonstrated in Figure 4, because significant <sup>13</sup>C or <sup>33</sup>S satellite lines were not observed in the EPR spectra. The pronounced spin-withdrawing effect of thiocarbonyl groups is due to the high polarizability of sulfur and is generally observed in radical anions exhibiting corresponding functionalities such as thioamides, thiono, and dithioesters.<sup>5b</sup> The spin density distribution of the bis-thiolester radical anion  $10^{\bullet-}$ , on the other hand, is not significantly different compared with that of the ester radical anion  $6^{\bullet-}$ .

Interestingly, the calculations yield different spin densities at the respective two chemically equivalent *ortho*-positions. This is due to the fact that an optimized, nearly coplanar conformation of the radical anion with the lowest potential energy is calculated. The dependence of the calculated (PM6) free enthalpy  $\Delta H$  from the torsion angle  $\Theta$  between the planes of the arene ring and the dithiocarboxylate group of  $3^{\bullet-}$  is shown in Figure 5.



**Figure 5** Dependence of the free enthalpy  $\Delta H$  on the torsion angle  $\Theta$  in 3<sup>•–</sup>.

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Global minima occur at  $\Theta_I = 0^\circ$  and  $\Theta_2 = 180^\circ$ , that is, for the coplanar configurations (strans is shown in Figure 4) with maximum resonance stabilization, together with a tiny local minimum ( $\Delta \Delta H = 4 \text{ kJ mol}^{-1}$ ) at  $\Theta_3 = 90^\circ$ , which is due to minimum steric hindrance between the *ortho*-protons and the functional group. The calculated average barrier height of  $\Delta \Delta H = 21 \text{ kJ mol}^{-1}$  between the two coplanar conformations with  $\Theta_I$  and  $\Theta_2$  obviously is low enough as to allow free rotation of the functional group at room temperature and to render the respective coupling constants indistinguishable on the EPR timescale.

Also, the spin density distribution and, as a consequence, the ring proton hfs coupling constants of  $3^{\bullet-}$  strongly depend on the torsion angle  $\Theta$  between the benzene ring and the dithioester group, which is illustrated in Figure 6. The best agreement of the MO (PM6) theoretical values  $\rho_{\mu}^{\pi}$  with the experimental values  $\rho_{\mu}^{\pi} = a^{\text{H}}/2.4$  is observed for torsion angles  $\Theta_{I} = 0^{\circ}$  and  $\Theta_{2} = 180^{\circ}$ . This coplanar arrangement, which also represents the



Figure 6 Dependence of the spin density distribution on the torsion angle  $\Theta$  in 3<sup>•-</sup>.

energetically favored conformation of  $3^{\bullet-}$  (see above), can however not be taken as a fixed conformation because free rotation occurs at room temperature. The spin densities  $\rho_{CS}^{S}$  and  $\rho_{CS}^{C}$  in the thiocarbonyl group of  $3^{\bullet-}$ , on the other hand, exhibit maxima at a fixed torsion angle  $\Theta = 90^{\circ}$  where virtually no resonance interaction between the arene ring and the functional group should exist.

#### CONCLUSION

Deuterium labeling of the OCH<sub>3</sub> and groups of  $3^{\bullet-}$  allows an unequivocal assignment of the respective proton hfs coupling constants with  $a^{\rm H}(\rm SCH_3) > a^{\rm H}(\rm OCH_3)$ .

MO calculations show that the spin density  $\rho_{3,5}^{\pi}$  in the *ortho*-positions next to the dithioester substituent is higher than  $\rho_{2,6}^{\pi}$  and thus  $a_{3,5}^{\text{H}} > a_{2,6}^{\text{H}}$  in  $3^{\bullet-}$ .

The spin density distribution in  $3^{\bullet-}$  as determined by MO calculations is compared with the one in the radical anions of the corresponding ester ( $6^{\bullet-}$ ), the asymmetric monothionoester ( $7^{\bullet-}$ ), the symmetric bisthionoester ( $8^{\bullet-}$ ), the tetrathioester ( $9^{\bullet-}$ ), and the bis-thiolester ( $10^{\bullet-}$ ). In agreement with the observed coupling constants and high *g*-factors, the spin densities  $\rho_{CS}^S$  and  $\rho_{CS}^C$  within the CS-SMe group are much higher compared with  $\rho_{CO}^\circ$  and  $\rho_{CO}^\circ$  within the CO-OMe substituents.

#### **EXPERIMENTAL**

**General procedure**. Melting points (mp, uncorrected) were determined on a Leitz-Heiztisch-Mikroskop. Column chromatography was performed on Kieselgel 60 (Merck, Darmstadt, Germany), 0.063–0.200 mm (70–230 mesh). Eluents [dioxan, petroleum ether (PE)] were distilled prior to use. Solvents were purified and dried by standard laboratory procedures.<sup>8</sup> IR spectra were measured as KBr pellets on a Perkin-Elmer 399 spectrometer. <sup>1</sup>H NMR spectra were measured in CDCl<sub>3</sub> on a Varian T 60 spectrometer. Chemical shifts  $\delta$  are related to SiMe<sub>4</sub> ( $\delta$  = 0.00 ppm) as internal standard. The radical anions were generated by internal electrolysis at 25 °C in dry and purified<sup>8</sup> DMSO with tetrapropylammonium bromide as a supporting electrolyte at -0.70 to -0.90 V versus the internal Ag/AgBr reference electrode.<sup>9</sup> The EPR spectra were measured as described<sup>5</sup> in a quartz flat cell on a Bruker ER 420 S spectrometer. They were simulated by use of the SYMFONIA program (Bruker).

#### Preparations

Methyl 4-cyanobenzoate (1) and 4-cyanobenzoyl chloride (Sigma-Aldrich, Buchs, Switzerland) as well as iodomethane- $d_3$  and methanol- $d_4$  (Merck) are commercially available.

**Trideuteromethanethiol.** Iodomethane- $d_3$  (16.1 g, 111 mmol) and thiourea (9.3 g, 122 mmol) were refluxed in EtOH (ethanol; 5 mL) for 6 h. *S*-Trideuteromethylisothiouronium iodide (24.2 g, 99%) crystallization from the solution upon cooling. It was filtered off, dried, and hydrolyzed with 5N NaOH (50 mL). The produced thiol was expelled from the solution by a stream of N<sub>2</sub> and trapped at -15 °C to yield trideuteromethanethiol as a colorless liquid (1.74 g, 31%).

**Trideuteromethyl 4-Cyanobenzoate (2).** 4-Cyanobenzoyl chloride (1.50 g, 9.1 mmol) was added portion-wise under stirring and cooling with ice to a solution of CD<sub>3</sub>OD

(0.32 g, 8.9 mmol) in dry pyridine (3.0 mL). The mixture was heated to  $80 \degree \text{C}$  for 30 min, poured into ice/water, and acidified with HCl. The slightly brown crystals of **2** (1.18 g, 81%) were filtered off, dried, and used without further purification.

**O,S-Dimethyl 4,4-Dithioterephthalate** {**Methyl 4-[(Methylthio)thiocarbon yl]benzoate**} (3). The dithioester 3 was prepared from 1 and unlabeled methanethiol as described for 5. Red leaflets, mp 87 °C–89 °C (lit.<sup>10</sup>: 90 °C). <sup>1</sup>H NMR:  $\delta$  2.75 (s, 3 H, SCH<sub>3</sub>), 3.90 (s, 3 H, OCH<sub>3</sub>), 8.00 (s, 4 H, ArH). Anal. Calcd. for C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>S<sub>2</sub> (226.3): C 53.07, H 4.45, S 28.34. Found: C 53.03, H 4.42, S 28.48.

S-Methyl O-Trideuteromethyl 4,4-Dithioterephthalate {Trideuteromethyl 4-[(methylthio)thiocarbonyl]benzoate} (4). The dithioester 4 was prepared from 2 (1.1 g, 6.7 mmol) and unlabeled methanethiol (0.75 mL) as described for 5. Red leaflets (0.35 g, 23%), mp 86 °C (lit.<sup>10</sup> for 3: 90 °C) <sup>1</sup>H NMR:  $\delta$  2.75 (s, 3 H, SCH<sub>3</sub>), 8.00 (s, 4 H, ArH). Anal. Calcd. for C<sub>10</sub>H<sub>7</sub>D<sub>3</sub>O<sub>2</sub>S<sub>2</sub> (229.5): C 52.38, H 3.08, D 2.62. Found: C 52.79, H 2.97, D 2.54.

**O-Methyl S-Trideuteromethyl 4,4-Dithioterephthalate {Methyl 4-[(Trideutero-methylthio)thiocarbonyl]benzoate}** (5). Trideuteromethanethiol (1.74 g, 2 mL, 34 mmol) was added to a solution of 1 (7.0 g, 43 mmol) in dry toluene (15 mL) at 0 °C. A stream of dry gaseous HCl was introduced into the solution at -10 °C. Losses of toluene were supplemented during the procedure. The solvent was removed by vacuum evaporation. The residue was dispersed in dry pyridine and a stream of H<sub>2</sub>S was introduced into the suspension at 0 °C for 4 h. The red colored reaction mixture was poured into ice and concd. aqu. HCl, and the mixture was extracted with CHCl<sub>3</sub>. The extract was dried and evaporated under vacuum to yield an oily red residue, which crystallized overnight. Column chromatography (dioxane/PE 15:85) gave red leaflets (1.3 g, 17%), mp 87 °C (lit.<sup>10</sup> for **3**: 90 °C). <sup>1</sup>H NMR:  $\delta$  3.95 (s, 3 H, OCH<sub>3</sub>), 8.00 (s, 4 H, ArH). Anal. Calcd. for C<sub>10</sub>H<sub>7</sub>D<sub>3</sub>O<sub>2</sub>S<sub>2</sub> (229.3): C 52.38, H 3.08, D 2.62, S 27.97. Found: C 52.35, H 3.02, D 2.58, S 27.97.

#### Calculations

Semiempirical PM6-type MO calculations were performed by use of the program package MOPAC 2009.<sup>7</sup> DFT-based geometry optimizations and spin density calculations were performed by the B3LYP method<sup>11</sup> with 6–31G(p,d) basis sets. The FIRE-FLY-program<sup>12</sup> was used for the DFT calculations. The QCPE programs DRAW and JMOL (Open Project; http://sourceforge.net/projects/jmol/) were used for the graphical presentation of the results. A conventional PC (Pentium Dual Core CPU E5200, 2.5 GHz; 3.25 GB RAM) was applied for the calculations.

#### REFERENCES

- EPR Studies on Carboxylic Esters, Part 21. For Part 20 see: Voss, J.; Kupczik, G.; Stahncke, H. J. Chem. Res. 2009, 283-286.
- (a) Voss, J.; Schlapkohl, K. *Tetrahedron* 1975, 31, 2982-2988; (b) Voss, J.; Schmüser, W.; Schlapkohl, K. J. Chem. Res. (S), 1977, 144-145, J. Chem. Res. 1977, (M), 1801-1830; (c) Edler, R.; Voss, J. Chem. Ber. 1989, 122, 187-191; (d) Debacher, U.; Schmüser, W.; Voss, J. J. Chem. Res. (S), 1982, 74-75, J. Chem. Res. (M), 1982, 876-892; (e) Voss, J.; Behrens, T.; Krasmann, M.; Osternack, K.; Prangova, L. J. Chem. Res. (S), 1997, 252-253.

- Voss, J.; Strey, K.; Maiboom, T.; Krasmann, M.; Adiwidjaja, G. Phosphorus Sulfur Silicon Relat. Elem. 2010, 185, 1273-1300.
- 4. Pesel, T. (PhD thesis: Darstellung von Azulencarbonsäureestern und Azulenthiocarbonsäureestern sowie ESR-spektroskopische Untersuchung ihrer Radikalanionen (Preparation of Azulenecarboxylic Acid Esters and Azulenethiocarboxylic Acid Esters, and ESR Spectroscopic Study of Their Radical Anions); University of Hamburg: Hamburg, 1996.
- (a) Gassmann, J.; Günther, H.; Osternack, K.; Thimm, K.; Voss, J. Magn. Reson. Chem. 1994, 32, 624-630; (b) Voss, J.; Bruhn, F.-R. Liebigs Ann. Chem. 1979, 1931-1944.
- 6. Hirayama, M. Bull. Chem. Soc. Jpn. 1967, 40, 1822-1826.
- Stewart, J. J. P. J. Mol. Mod. 2007, 13, 1173-1213. http://www.springerlink.com/content/ ar33482301010477/fulltext.pdf (accessed 02.05.2011). We thank Prof. Stewart for providing us with the newest version MOPAC 2009 for our calculations.
- Becker, H. G. O.; Berger, W.; Domschke, G.; Fanghänel, E.; Faust, J.; Fischer, M.; Gentz, F.; Gewald, K.; Gluch, R.; Mayer, R.; Müller, K.; Pavel, D.; Schmidt, H.; Schollberg, K.; Schwetlick, K.; Seiler, E.; Zeppenfeld, G. Autorenkollektiv, *Organikum*, 19th ed.; Johann Ambrosius Barth: Leipzig, Berlin, Heidelberg, 1993.
- ΔE = -520 mV versus the SCE. (a)Voss, J.; Edler, R. J. Chem. Res. 2007, 226-228; (b) Günther, H.; Voss, J. J. Chem. Res. (S), 1987, 68-69, J. Chem. Res. 1987, (M), 775–789.
- 10. Mayer, R.; Scheithauer, S.; Kunz, D. Chem. Ber. 1966, 99, 1393-1413.
- (a) Becke, A. D. Phys. Rev. 1988, A38, 3098-3100; (b) Becke, A. D. J. Chem. Phys. 1992, 97, 9173-9177.
- Firefly QC package, Granovsky, A. A. Firefly version 7.1.G, www http://classic.chem.msu.su/gran/ firefly/index.html (access date: 08.04.2011), which is partially based on the GAMESS (US) source code; Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. J. Comput. Chem. **1993**, 14, 1347-1363.

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