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EPR studies on carboxylic esters. Part 17.[1] EPR spectra and spin densities in the radical anions of thio and dithiocoumarins

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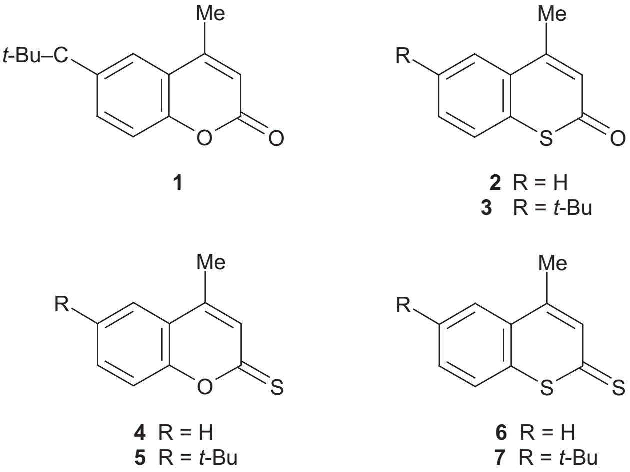
The radical anions of 4-methyl-1-thiocoumarins and 4-methyl-1-thio-2-thionocoumarins are generated by internal electroreduction and studied by EPR spectrosopy. The spin density distribution is evaluated from the proton hfs coupling constants and by MO calculations. The radical anions of the corresponding coumarins and 2-thionocoumarins are not persistent enough for EPR spectroscopic measurements.

Keywords: coumarins, thiocoumarins, dithiocoumarins, EPR spectroscopy, spin densities

In continuation of our earlier studies on 2*H*-thiopyrane-2-thione radical anions,[2] we present here results on the related benzo derivatives, the thiocoumarin radical anions. Thiocoumarins can be considered as cyclic thiocinnamic esters. The latter are known to give persistent radical anions only if they are substituted at the β-position, which exhibits the highest spin density.[3] As a result, unsubstituted cinnamic as well as acrylic derivatives easily undergo hydrodimerisation at the β-position.[4] The same is obviously true for coumarins and thiocoumarins without a substituent in the 4-position, the radical anions of which are unstable according to a preliminary study. We chose, therefore, the sterically protected 4-methylcoumarin derivatives for our investigation.

Results and discussion

Cyclovoltammetric half-wave potentials $E_{1/2}$ corresponding to the single electron transfer (SET) step of the coumarin **1**, and the thio- and dithiocoumarins **2**–**7** (Scheme 1), which we have studied, are compiled in Table 1. They were determined in a solution of tetrapropylammonium bromide in dry DMF at the dropping mercury electrode. A silver wire served as internal reference electrode. This system exhibits the reproducible potential of the Ag/Ag$^+$/AgBr/Br$^-$ chain in the solvent supporting electrolyte (ΔE = –520 mV *vs* the SCE)[5] and is also very suitable for the *in situ* generation of radical anions.[1,5,6]



1

2 R = H
3 R = *t*-Bu

4 R = H
5 R = *t*-Bu

6 R = H
7 R = *t*-Bu

Scheme 1

Table 1 Polarographic reduction potentials $E_{1/2}$ (V)[a] and peak current ratios i_{ap}/i_{cp}[b]

Compound	$E_{1/2}$ (V)[a]	i_{ap}/i_{cp}
1	–1.34	No anodic peak
2	–1.13	0.45
3	–1.17	0.37
4	–0.75	No anodic peak
5	–0.84	No anodic peak
6	–0.66	0.54
7	–0.71	0.40

[a] *versus* the internal Ag/Ag$^+$/AgBr/Br$^-$ reference electrode; [b] according to ref. [4], measured at a sweep rate of 500 mVs^{-1}.

The reduction potentials $E_{1/2}$ of the thiocarbonyl derivatives **4**–**7** are shifted in the positive direction as compared with $E_{1/2}$ of the carbonyl derivatives **1**–**3**. This is not unexpected since the former can be considered as cyclic thiono and dithioesters whereas the carbonyl derivatives represent ester and thiolester type compounds. The shift is due to the enhanced polarisability of the thiocarbonyl group and has been observed in many cases of open-chained thiono and dithioesters too.[7] The ratios i_{ap}/i_{cp} of the anodic and the cathodic peaks are indicative of the reversibility of the SET step, *i.e.*, the lifetime of the radical anions.[8] As a rule of thumb one can assume that radical anions will be persistent enough as to give EPR spectra with a sufficient signal-to-noise ratio at or slightly below room temperature if $i_{ap}/i_{cp} > 0.4$.

Accordingly, we could indeed record well-resolved EPR spectra of the radical anions of **2**, **3**, **6** and **7**. Figure 1 shows, for instance, the experimental EPR spectrum of the radical anion of **2** together with the corresponding simulation.

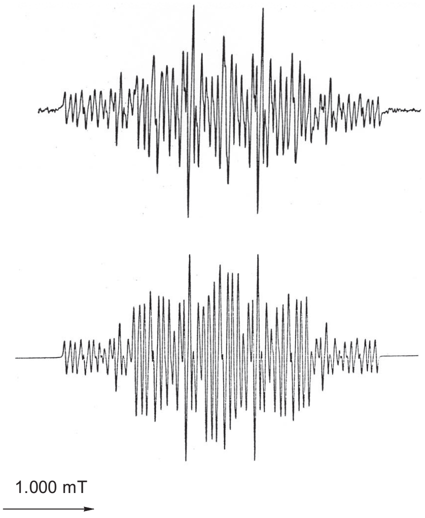


Fig. 1 Experimental (top) and simulated (bottom) EPR spectrum of the 4-methyl-1-thiocoumarin (**2**) radical anion.

We were, however, not able to detect the radical anions of **1**, **4**, or **5**, even when we performed the measurements at –80°C (in a 1:1 mixture of DMF and acetonitrile). Obviously, the persistency, *i.e.* the kinetic stability, of the radical anions is decisively enhanced by the presence of a sulfur centre in

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Table 2 Proton hfs coupling constants a^H_μ (mT) and *g*-factors of the thiocoumarin radical anions $\mathbf{2}^{\cdot-}$, $\mathbf{3}^{\cdot-}$, $\mathbf{6}^{\cdot-}$ and $\mathbf{7}^{\cdot-}$

Compound	*a*(3-H)	*a*(5-H)	*a*(6-H)	*a*(7-H)	*a*(8-H)	*a*(CH_3)	*g*-factor
2	0.206	0.343	0.114	0.493	0.065	0.775	2.00410
3	0.196	0.332	–	0.426	0.070	0.820	2.00412
6	0.111	0.277	0.091	0.299	0.041	0.934	2.00593
7	0.138	0.283	–	0.310	0.047	0.972	2.00580

the coumarin system although the one-electron reduction of thionocoumarins is achieved at less negative reduction potentials (Table 1), which should be indicative of a higher thermodynamic stability of the radical anions compared with the corresponding carbonyl derivatives.

The proton hyperfine coupling constants a^H_μ and *g*-factors are given in Table 2.

The determination of the expected six different proton hfs coupling constants from up to observed 116 of the principally possible 128 (4×2^5) lines in the EPR spectra was not trivial. The large quadruplet splittings resulting from the methyl protons as well as the smallest doublet splittings in the wings of the spectra were easy to detect. We have determined the missing four doublet splittings of medium size by use of the autocorrelation function and simulation of the spectra (see Fig. 1).[9]

Also the assignment of the five doublet splittings to specific protons was a difficult task. The coupling constants of the protons in the 6-positions of **2** and **3** were identified by comparison with the spectra of the corresponding 6-*t*-butyl derivatives **6** and **7**. Due to the well established presumption that the disturbance of the spin density distribution and hence a change of the proton coupling constants by *t*-butyl groups are not significant,[2,6,10] the splittings of 6-H in **2** and **3** disappeared in the spectra of **6** and **7** since the small γ-splittings of the *t*-butyl protons are not resolved.

The two larger ones of the remaining for coupling constants were tentatively assigned to 5-H and 7-H. From a qualitative point of view these positions should exhibit high spin densities and, accordingly, large proton hfs coupling constants since reasonable resonance formulae of the radical anions without octet extension are only possible with a free spin in the 4-, 5-, and 7-position (Scheme 2).

This assignment was also supported by HMO calculations with McLachlan refinement,[11] which gave *a*(5-H) = 0.24 mT and *a*(7-H) = 0.32 mT for **2**, and *a*(5-H) = 0.25 mT and *a*(7-H) = 0.30 mT for **6** by use of the McCONNELL equation $a^H_\mu = Q \cdot \rho^\pi_\mu$ (Q = –2.2 mT). The HMO calculation of *a*(6-H) and *a*(8-H) gave values lower than 0.1 mT in agreement with the observed two small splittings, whereas *a*(3-H) = 0.31 mT (HMO) for **6** does not agree with the experimental value of 0.11 mT. Obviously, considerable spin densities are also present in the less favourable positions, which can be made plausible by resonance formulae with electron decets at the sulfur centre (Scheme 2). A precise estimation of the coupling constants by simple HMO calculations is, however, not possible and a completely reliable assignment on this basis is thus not reasonable.[12]

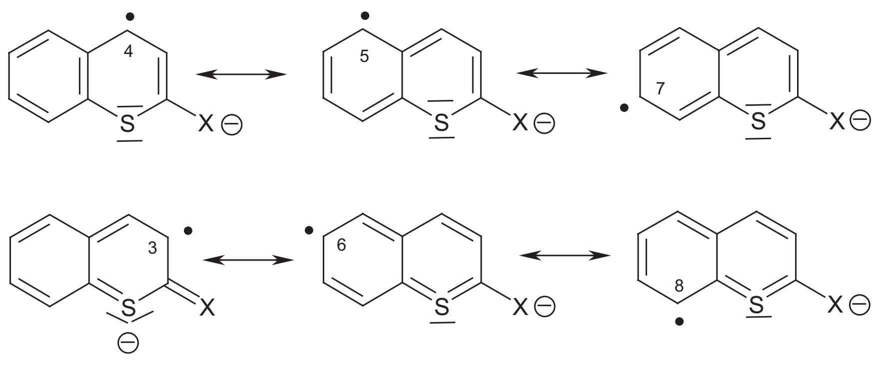
We have therefore confirmed the considerations on the π-spin densities by *semi*-empirical MNDO/CI type MO calculations for the radical anion of **6**. The results are given in Table 3. The obvious agreement with the experimental coupling constants allows a convincing assignment. Expectedly, also *a*(6-H) the assignment of which is unequivocal on account of the comparison between **6** and **7** is reproduced correctly. Interestingly, the spin densities at the 3- and 4-position of **6** are very similar to those calculated for the corresponding positions in 2*H*-thiopyrane-2-thione radical anions.[2] Even the radical anions of *O*-ethyl 3-methyl-3-aryl-propenethioates [Ar–C(CH_3)=CH–CS–OEt], the open-chained analogs of thiocoumarin, exhibit quite similar spin density distributions.[3]

According to general experience, the protons of freely rotating methyl groups at a centre *μ* of an aromatic π-electron system exhibit hfs coupling constants $a^H(CH_3)$ of the same order of magnitude as protons bound directly to the centre *μ*, provided the π-spin densities ρ^π_μ at *μ* do not differ

Table 3 Spin densities ρ^π_μ[a], and calculated[b] and experimental proton hfs coupling constants a^H_μ (mT) in the dithiocoumarin radical anions $\mathbf{6}^{\cdot-}$ and $\mathbf{7}^{\cdot-}$

Centre *μ*	ρ^π_μ (**6**)[a]	a^H_μ (**6**), calcd.[b]	a^H_μ (**6**), exp.	a^H_μ (**7**), exp.
3	+0.060	–0.132	0.111	0.138
4	+0.338	+0.980[c]	0.934	0.972
5	+0.146	–0.321	0.277	0.283
6	–0.048	+0.106	0.091	–
7	+0.168	–0.370	0.299	0.310
8	–0.021	+0.046	0.041	0.047

[a] MNDO/CI; [b] $a^H_\mu = -2.2\ \rho^\pi_\mu$; [c] $a^H(CH_3) = +2.9\ \rho^\pi_4$.[13]



Scheme 2

significantly.[12] This effect is mainly due to hyperconjugation and is observed in the thiocoumarin radical anions too (see Table 3).

Although an exact calculation of $a^{H}(CH_3)$ by use of a simple equation $a^{H}(CH_3) = Q_{CCH3}\cdot\rho^{\pi}_{\mu}$ is problematic since Q_{CCH3} is not a constant but depends on ρ^{π}_{μ}[12] a rough estimation with $Q_{CCH3} = 2.9$ mT[13] gives $a^{H}(CH_3) = 0.980$ mT which is in reasonable agreement with the experimental value of 0.934 mT for the radical anion of **6**.

The calculation of π-spin densities ρ^{π}_{μ} from *g*-factors is not straightforward although a quantitative relationship between ρ^{π}_{μ}, *g*, the spin-orbit coupling constant ζ, and the electronic excitation energy $\Delta E(n\rightarrow\pi^*)$ exists.[14] However, $\Delta E(n\rightarrow\pi^*)$ of radical anions is not easy to determine. Furthermore, the correct symmetry of the *g*-tensor must be known and taken into account. The data in Table 2 show that the dithiocoumarins exhibit markedly higher *g*-factors than 1-thiocoumarins. This is due to the heavy-atom effect of the thiocarbonyl sulfur ($\zeta_S = -382$ cm^{-1}). It is, in a semi-quantitative sense, indicative of a significant π-spin density in the thiocarbonyl group. The same increase of *g*-factors has been observed and discussed for benzoate esters and benzamides, and the corresponding sulfur and selenium analogs.[3,5,6,7a,7b,15]

Experimental

The compounds **1**,[16] **2**,[17] **3**,[16] **4**,[16,18] **5**,[16] **6**[19] and **7**[16] were prepared as described in the cited literature.

Polarograms and cyclic voltamograms of solutions containing 10^{-3} moll^{-1} of substrate and 0.1 moll^{-1} of tetrapropylammonium bromide in dry DMF were measured with a Bruker polarograph E 310. The internal Ag/Ag^{+}/AgBr/Br^{-} reference electrode which we used exhibits a potential shift of –520 mV *vs* the SCE.[5] Radical anions were generated by *in situ* electroreduction in a quartz flat cell at appropriate potentials by use of a Wenking MP 31 potentiostat in the same solvent-supporting electrolyte. The EPR spectra were recorded, in general at room temperature, on a Bruker 420s spectrometer (X-band).[1,5,6,7] The *g*-factors were calibrated against the perylene radical cation ($g = 2.002564$).[20]

HMO calculations were performed by use of the online program SHMO.[11] The modified program package MNDOC (QCPE-Version, program nr. 438) was used for the MNDO calculations.[21]

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References

1 Part 16. T. Behrens, S. Bruns and J. Voss, *J. Phys. Org. Chem*., 2000, **13**, 624.
2 R. Röske and J. Voss, *Phosphorus Sulfur*, 1986, **26**, 257.
3 (a) W. Schmüser, Ungesättigte Carbonyl- und Thiocarbonylverbindungen.—ESR-spektroskopische Untersuchungen ihrer Radikalanionen, PhD thesis, University of Hamburg, 1979; (b) R. Spohnholz, Stereoselektive Darstellung vinyloger Benzolcarbonsäureester und Untersuchungen zur Elektronenübertragung, PhD thesis, University of Hamburg, 1990.
4 L.H. Klemm and R.D. Olson, *J. Org. Chem*., 1973, **38**, 3390.
5 H. Günther and J. Voss, *J. Chem. Res*., 1987 (*S*) 68; (*M*) 775.
6 J. Voss and F.-R. Bruhn, *Liebigs Ann. Chem*., 1979, 1938.
7 (a) J. Voss and K. Schlapkohl, *Tetrahedron*, 1975, **31**, 2982; (b) U. Debacher, W. Schmüser and J. Voss, *J. Chem. Res*., 1982 (*S*) 74; (*M*) 876; (c) L. Prangova, T. Strelow and J. Voss, *J. Chem. Res*., 1985 (*S*) 118; (*M*) 1401; (d) L.S. Prangova, A. Böge, B. Wollny and J. Voss, *J. Chem. Res*., 1987 (*S*) 182; (*M*) 1601; (e) L. Prangova, K. Osternack and J. Voss, *J. Chem. Res*., 1995 (*S*) 234; (*M*) 1551.
8 (a) R. Nicholson and I. Shain, *Anal. Chem*., 1964, **36**, 706; (b) R.S. Nicholson, *Anal. Chem*., 1966, **38**, 1406.
9 I. Büchel and J. Voss, *unpublished results*, Univ. Hamburg, 1982; F. Schneider and M. Plato, *Elektronenspinresonanz*, Thiemig, München, 1972, p. 182f.
10 I.B. Goldberg and B.M. Peake, *J. Phys. Che*m., 1977, **81**, 571.
11 R. Cannings, *Simple Huckel Molecular Orbital, SHMO*, an iterative online program (http: //www.chem.ucalgary.ca/SHMO/), based on: A. Rauk, *Orbital Interaction Theory of Organic Chemistry*, chapters 3 and 5, Wiley Interscience, Chichester, 1994.
12 (*a*) F. Gerson, *Hochauflösende ESR-Spektroskopie*, Verlag Chemie, Weinheim, 1967; (*b*) F. Gerson and W. Huber, *Electron Spin Resonance Spectroscopy of Organic Radicals*, Wiley-VCH, Weinheim, 2003.
13 I.H. Elson and T.J. Kemp, *J. Chem. Soc., Faraday Trans. 2*, 1973, 1402.
14 (a) H.M. McConnell and R.E. Robertson, *J. Phys. Chem*., 1957, **61**, 1018; (b) H.C. Heller, *J. Am. Chem. Soc*., 1967, **89**, 4288.
15 J. Voss, W. Schmüser and K. Schlapkohl,, *J. Chem. Res*., 1977 (*S*) 144; (*M*) 1801.
16 J. Voss, R. Edler and G. Adiwidjaja, *Phosphorus, Sulfur, Silicon*, 2007, **182**, in press.
17 H. Nakazumi, A. Asada and T. Kitao, *Chem. Lett*., 1979, 387; *Bull. Chem. Soc. Jpn*., 1980, **53**, 2046.
18 (a) K. Ito and K. Nakajima, *J. Heterocycl. Chem*., 1988, **25**, 511; (b) A.C. Williams and N. Camp, *Science of Synthesis*, ed. R.J. Thomas, Thieme Verlag, Stuttgart, 2003, Vol. 14, p.443.
19 H. Nakazumi and T. Kitao, *Bull. Chem. Soc. Jpn*, 1977, **50**, 939; 1980, **53**, 2415.
20 R.D. Allendoerfer, *J. Chem. Phys*., 1971, **55**, 3615.
21 W. Thiel, *J. Am. Chem. Soc*., 1981, **103**, 1413.