EPR studies on carboxylic esters. Part 20. EPR spectra and spin densities in radical anions of isocoumarin, benzocoumarin and their sulfur analogues

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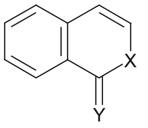
The radical anions of isocoumarin, benzocoumarin and the six corresponding sulfur analogues have been generated by internal electroreduction and studied by EPR spectrosopy. The spin density distributions have been evaluated from the proton hyperfine structure coupling constants and by MO calculations. They are discussed with respect to the spin density distributions in related radical anions.

Keywords: isocoumarin, benzocoumarin, thio-isocoumarins, thio-benzocoumarins, EPR spectroscopy, spin densities

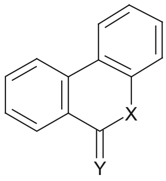
Recently we have reported on the radical anions of coumarins and their sulfur analogues,[1,2] which may be thought of as cyclic cinnamate esters and thioesters. Their isomeric counterparts, the isocoumarins, on the other hand, represent *cyclo*-conjugated benzoate esters and thioesters, whereas the corresponding benzoanellated derivatives exhibit a combination of both these features. Accordingly, this should be reflected in the spin density distributions. We have therefore prepared these compounds and studied the EPR spectra of their radical anions in order to corroborate these considerations by experimental evidence.

Results and discussion

The compounds to study, **1**–**8**, were prepared according to literature procedures (see Experimental).



1: X = Y = O
2: X = S, Y = O
3: X = O, Y = S
4: X = Y = S



5: X = Y = O
6: X = S, Y = O
7: X = O, Y = S
8: X = Y = S

Their polarographic half-wave reduction potentials $E_{½}$ corresponding to the formation of radical anions by single electron transfer (SET) of **1**–**8**, which we have determined as described earlier,[2–4] are compiled in Table 1.

A continuous shift of $E_{½}$ into the positive direction is observed in the two series **1** → **2** → **3** → **4** and **5** → **6** → **7** → **8** of the compounds. This shift can be explained by the enhanced polarisability of sulfur as compared with oxygen and, in particular, of the thiocarbonyl group *versus* the carbonyl group, which facilitates the uptake of an electron into the molecule. We have observed this effect also in the coumarin series[2] and in open-chain esters and their sulfur analogues.[5–9] Furthermore, a significant shift in the same direction occurs between the isocoumarins **1**–**4** and the corresponding benzocoumarins **5**–**8**. This effect should be due to the more extended π-electron system of the latter with a smaller HOMO–LUMO difference. Remarkably, the reduction potentials $E_{½}$ of the benzocoumarins are similar to $E_{½}$ of the corresponding coumarin derivatives[2] whereas the $E_{½}$-values of the isocoumarins deviate significantly. Thus, in terms of the SET step, the benzocoumarin system is obviously more closely related to the coumarin than to the isocoumarin system, each of which formally represents a constituent of the benzocoumarin system.

Table 1 Polarographic reduction potentials $E_{½}/\mathrm{V}^{a}$ and peak current ratios $i_{ap}/i_{cp}{}^{b}$

Compound	$E_{½}/\mathrm{V}^{a}$	$i_{ap}/i_{cp}{}^{b}$
1	–1.41	0.43
2	–1.27	0.43
3	–1.07	0.47
4	–0.72	0.77
5	–1.32	0.90
6	–1.16	1.04
7	–0.68	0.72
8	–0.58	c

[a] *vs* the internal Ag/Ag+/AgBr/Br– reference electrode in dry DMF, the potential of which is shifted by –520 mV *vs* the SCE according to ref. 3; [b] according to refs 10,11 measured at a sweep rate of 500 mVs–1; [c] no anodic peak observed.

With the exception of **8**, the ratios i_{ap}/i_{cp} of the anodic and the cathodic peaks[10,11] (Table 1) are well above 0.4. This is, in general, indicative of the formation of radical anions which are sufficiently persistent for EPR measurements at ambient temperature.

Accordinglyly, we could record well-resolved EPR spectra with high signal-to-noise ratios as exemplarily illustrated for the radical anions of isocoumarin **1** (Fig. 1), thioloisocoumarin **2** (Fig. 2), thionobenzocoumarin **7** (Fig. 3) and dithiobenzocoumarin **8** (Fig. 4). Fortunately, this even holds for the dithiobenzocoumarin **8** (see Fig. 4) although **8** does not exhibit an anodic counter peak in its cyclovoltamogram (Table 1). This unexpected result may be due to the different geometries of the cells and different time-scales of the cyclovoltammetric and the EPR measurements and is observed occasionally.

The isocoumarin radical anions and their sulfur analogues $\mathbf{1}^{-\bullet}$ – $\mathbf{4}^{-\bullet}$ exhibit *g*-factors close to the values of the respective benzocoumarin radical anions $\mathbf{5}^{-\bullet}$ – $\mathbf{8}^{-\bullet}$. They are similar to those found in the coumarin series.[2] Due to the heavy-atom effect of the thiocarbonyl sulfur, *i.e.* its high spin-orbit coupling constant $\xi = -382\ \mathrm{cm}^{-1}$, the *g*-factors of $\mathbf{3}^{-\bullet}$, $\mathbf{4}^{-\bullet}$, $\mathbf{7}^{-\bullet}$ and $\mathbf{8}^{-\bullet}$ are markedly higher than these of $\mathbf{1}^{-\bullet}$, $\mathbf{2}^{-\bullet}$, $\mathbf{5}^{-\bullet}$ and $\mathbf{6}^{-\bullet}$. The data are, in a semi-quantitative sense, indicative of significant spin densities in the thiocarbonyl groups of the thiono and dithio derivatives, although a precise and conclusive calculation of $\rho^{\pi}(\mathrm{C{=}S})$ from the *g*-factors is not possible.

The proton hyperfine structure (hfs) coupling constants a^{H}_{μ} could be determined exactly by use of the autocorrelation function[2,12] and simulation of the spectra in spite of the fact that due to the low symmetry of the molecules the number of different hfs splittings and consequently the number of lines is rather large. The coupling constants and *g*-factors of $\mathbf{1}^{-\bullet}$ – $\mathbf{8}^{-\bullet}$ are compiled in Table 2.

In the case of $\mathbf{6}^{-\bullet}$, $\mathbf{7}^{-\bullet}$ and $\mathbf{8}^{-\bullet}$ several protons appear as accidentally equivalent. The assignment of the coupling constants a^{H}_{μ} to distinct protons was achieved through

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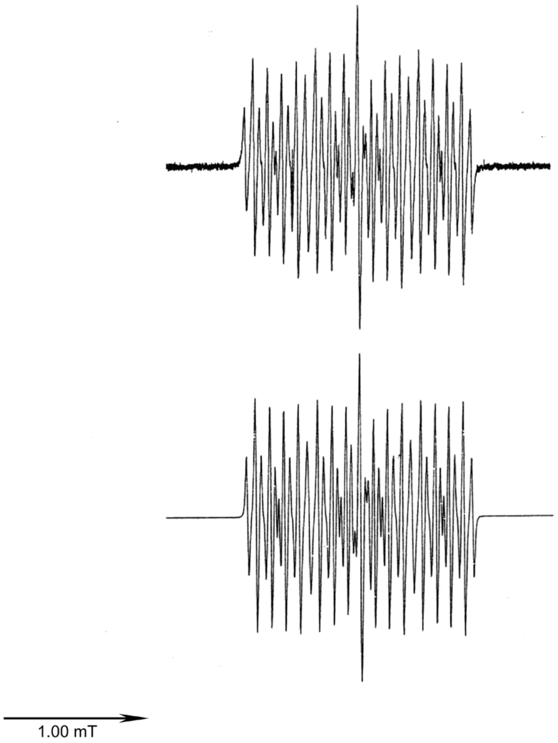


Fig. 1 Experimental (top) and simulated (bottom) EPR spectrum of the isocoumarin radical anion ($\mathbf{1}^{-\bullet}$).

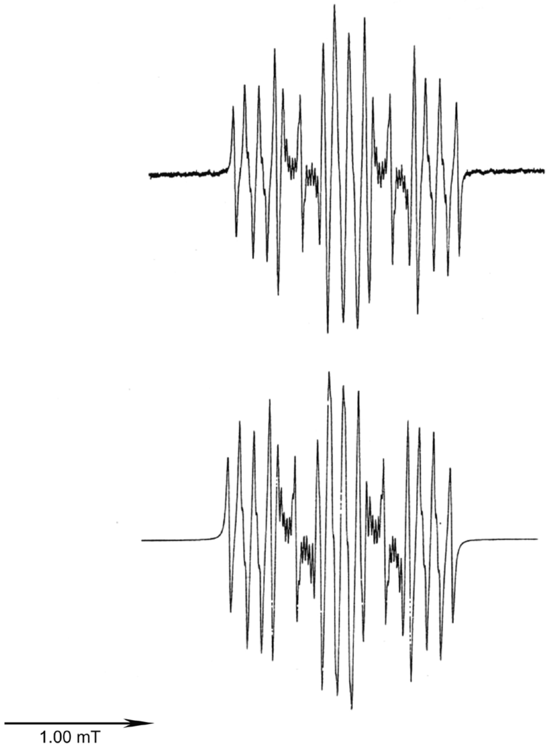


Fig. 2 Experimental (top) and simulated (bottom) EPR spectrum of the thioloisocoumarin radical anion ($\mathbf{2}^{-\bullet}$).

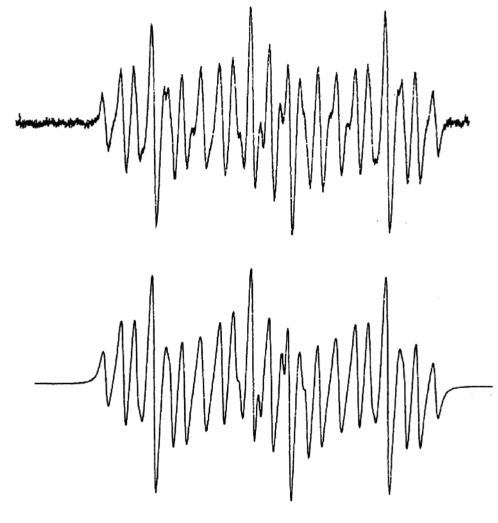


Fig. 3 Experimental (top) and simulated (bottom) EPR spectrum of the thionobenzocoumarin radical anion ($\mathbf{7}^{-\bullet}$).

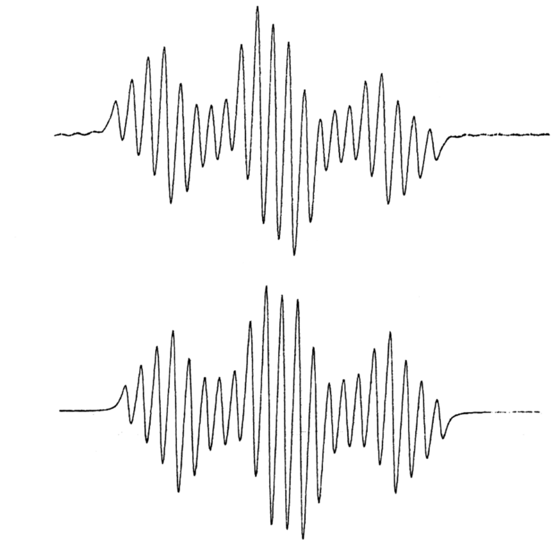
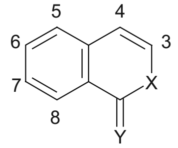


Fig. 4 Experimental (top) and simulated (bottom) EPR spectrum of the dithiobenzocoumarin radical anion ($\mathbf{8}^{-\bullet}$).

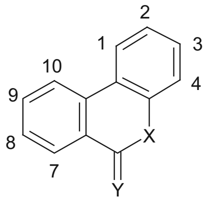
comparison of the experimental data with values calculated from McLachlan type HMO spin densities $\rho^\pi{}_\mu$ by application of the McConnell equation $a^H{}_\mu = -2.7\rho^\pi{}_\mu$ (*cf.* Table 3).

On the whole, the agreement between the theoretical and experimental spin densities is quite satisfactory. The assignment of the very low values close to zero is of course, somewhat arbitrary but this fact does not affect the discussion of the spin density distributions significantly. There are however some more significant deviations. In particular, $\rho^\pi{}_8$ is overestimated for the carbonyl derivatives **1** and **2**. This may be due to a reduced resonance interaction between the carbonyl groups of **1** and **2** and the adjacent benzene rings as compared with open-chain benzoic esters from which the parameters *k* and *h* of the Coulomb and resonance integrals are taken (see Experimental). In fact, an improved agreement for $\rho^\pi{}_8$ was achieved by use of a lower resonance integral $k_{C1\text{-}C8a} = 1.1$ instead of 1.2. On the other hand, $\rho^\pi{}_6$ results as too large for the thiocarbonyl derivatives **3** and **4**, which could also be adjusted by choice of lower resonance parameters $k_{C1\text{-}C8a} = 0.9$ (**3**) and 1.1 (**4**) and a higher resonance parameter $k_{C=S} = 1.23$ instead of 0.77 for **3** (*cf.* Table 4). The highest spin densities are found in the 6- and 8-positions with $\rho^\pi{}_6 > \rho^\pi{}_8$, which positions are equivalent to the *para*- and *ortho*-positions in open-chain benzoate esters and thioesters.[5–9] Considerable spin densities

Table 2 Proton hfs coupling constants a^H_μ/mT and *g*-factors of the radical anions of



1 – 4

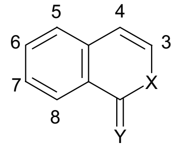


5 – 8

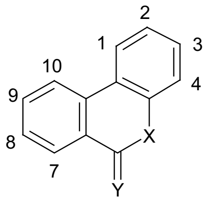
Compound	a^H_μ/mT								*g*-factor
	a(3-H)	*a*(4-H)	*a*(5-H)	*a*(6-H)	*a*(7-H)	*a*(8-H)			
1	0.214	0.067	0.063	0.780	0.110	0.467			2.00335
2	0.304	0.105	0.084	0.652	0.125	0.364			2.00435
3	0.148	0.087	0.020	0.636	0.150	0.465			2.00457
4	0.138	0.098	0.044	0.518	0.159	0.414			2.00644
	a(1-H)	*a*(2-H)	*a*(3-H)	*a*(4-H)	*a*(7-H)	*a*(8-H)	*a*(9-H)	*a*(10-H)	
5	0.299	0.045	0.171	0.124	0.171	0.015	0.535	0.149	2.00389
6	0.297	0.047	0.147	0.047	0.171	0.027	0.589	0.123	2.00413
7	0.128	[a]	0.074	[a]	0.415	0.047	0.572	0.128	2.00476
8	0.122	[a]	0.061	[a]	0.359	0.061	0.482	0.122	2.00637

[a]Not resolved.

Table 3 Experimental ($\rho^\pi_\mu = a^H_\mu/-2.7$) and *theoretical*[a] (HMO) spin densities ρ^π_μ in the iso- and benzocoumarin radical anions



$1^{-\bullet}$ – $4^{-\bullet}$



$5^{-\bullet}$ – $8^{-\bullet}$

Compound	ρ^π_μ at centre μ							
	3	4	5	6	7	8		
1	0.079	0.025	0.023	0.289	0.041	0.173		
	0.097	*–0.037*	*–0.010*	*0.297*	*–0.053*	*0.185*		
2	0.113	0.039	0.031	0.241	0.046	0.135		
	0.115	*–0.046*	*–0.027*	*0.243*	*–0.041*	*0.137*		
3	0.055	0.032	0.007	0.235	0.056	0.172		
	0.056	*–0.026*	*–0.008*	*0.247*	*–0.057*	*0.178*		
4	0.051	0.036	0.016	0.192	0.059	0.153		
	0.057	*–0.032*	*–0.016*	*0.184*	*–0.057*	*0.154*		
	1	2	3	4	7	8	9	10
5	0.111	0.017	0.064	0.046	0.067	0.006	0.198	0.055
	0.124	*–0.023*	*0.080*	*0.046*	*0.082*	*0.006*	*0.198*	*–0.062*
6	0.110	0.017	0.054	0.017	0.064	0.010	0.218	0.046
	0.110	*–0.024*	*0.078*	*0.034*	*0.086*	*–0.006*	*0.190*	*–0.058*
7	0.047	[b]	0.027	[b]	0.154	0.027	0.212	0.047
	0.064	–0.012	*0.040*	0.017	*0.157*	*–0.050*	*0.183*	*–0.053*
8	0.045	[b]	0.023	[b]	0.133	0.023	0.178	0.045
	0.060	–0.013	*0.038*	0.014	*0.134*	*–0.045*	*0.164*	*–0.051*

[a]Shown in *Italics*. [b]No couplings observed, see Table 2.

exist, however, also in the 7-position, which may be regarded as a *meta*-position in a benzoate ester. Furthermore, ρ^π_3 is significantly non-zero too. This is not unexpected because the 3-position in an isocoumarin corresponds with the 6-position in a 2*H*-thiopyrane-2-thione, and we have found $a^H_6 = 0.69$ mT and $\rho^\pi_6 = 0.256$ for the radical anion of 5-*tert*-butyl-2*H*-thiopyrane-2-thione.[13] Thus, the general order of the spin densities in the radical anions of the isocoumarins **1**–**4** is $\rho^\pi_6 > \rho^\pi_8 > \rho^\pi_3 \approx \rho^\pi_7$. This spin density distribution is different from the situation in the coumarin radical anions, which obviously can be considered as cyclic cinnamic acid derivatives and exhibit thus the highest spin densities in the 7- and the 5-positions.[2]

In the benzocoumarin series, the calculated spin density ρ^π_1 comes out too high for **5** and the calculated ρ^π_9 values are too low for **6**–**8** as compared with the experimental values although we used Coulomb integrals for the exocyclic heteroatoms [h_O(**5**) = 1.65; h_O(**6**) = 0.6; h_S(**8**) = 0.25] which were slightly different from the parameters given in the literature (*cf.* Table 4). More spin density is located in the rings adjacent

Table 4 Coulomb (k) and resonance parameters (h) used for the McLachlan type MO calculations

Parameter[a]	1	2	3	4	5	6	7	8
k(C = X)	1.6	1.1	1.23	0.7	1.6	1.2	0.77	0.66
k(C–Y)	1.2	0.8	0.68	0.8	1.1	0.9	0.54	0.65
k(C–C)[b]	1.1	1.1	0.90	1.1	1.2	1.2	1.2	1.2
h_X(C = X)	1.5	0.2	0.62	0.0	1.65	0.6	0.5	0.25
h_Y(C–Y)	2.1	1.8	1.54	2.0	2.0	2.0	1.5	1.9

[a] X = O for **1**, **2**, **5**, **6**; X = S for **3**, **4**, **7**, **8**; Y = O for **1**, **3**, **5**, **7**; Y = S for **2**, **4**, **6**, **8**. [b] C1–C8a for **1**–**4**; C6–C6a for **5**–**8**.

to the carbonyl or thiocarbonyl double bond as compared with the other annelated benzene ring. Thus, the spin density distributions in the benzocoumarin radical anions with $\rho^{\pi}_{9} > \rho^{\pi}_{1} > \rho^{\pi}_{3} \approx \rho^{\pi}_{7}$ for $\mathbf{5}^{-\bullet}$ and $\mathbf{6}^{-\bullet}$, and $\rho^{\pi}_{9} > \rho^{\pi}_{7} > \rho^{\pi}_{1}$ for $\mathbf{7}^{-\bullet}$ and $\mathbf{8}^{-\bullet}$ resemble those in the isocoumarin radical anions if one considers that the 6- and 8-positions in **1**–**4** correspond with the 9- and 7-positions in **5**–**8**. This is to be expected because the benzocoumarins can be regarded as intramolecular phenyl benzoates and thiobenzoates. Considerable spin density is, however, also found in the second ring since the benzocoumarins may also be regarded as biphenyl derivatives with an observed hfs coupling constant of *e.g.* 0.32 mT for the 4'-proton in the *tert*-butyl biphenyl-4-carboxylate radical anion.[14]

Experimental

Isocoumarin (isochromen-1-one, **1**) was prepared from homophthalic acid [(2-carboxyphenyl)ethanoic acid] and ethyl formate. White needles, m.p. 44–46 °C (petroleum ether), lit.[15]: 45–46 °C. Thiolo-isocoumarine (thioisochromen-1-one, **2**) was obtained from 2-formylbenzoic acid. Light-yellow needles, m.p. 78–80 °C (petroleum ether), lit.[16]: 78–79 °C. Thiono-isocoumarin (isochromene-1-thione, **3**) was prepared by thionation of **1** with Lawesson's reagent[17,18] in toluene instead of P_4S_{10}.[19,20] Yellow needles, m.p. 106–107 °C (EtOH), lit.[19,20]: 106 °C. Dithio-isocoumarin (thioisochromene-1-thione, **4**) was prepared by thionation of **2** with Lawesson's reagent[17,18] in toluene instead of P_4S_{10}.[21] Red needles (68% yield), m.p. 88–89 °C (EtOH). Found: C, 60.66; H, 3.33; S, 36.10. Calcd for $C_9H_6S_2$ (178.28), C, 60.63; H, 3.39; S, 35.97%. ^{1}H and ^{13}C NMR in agreement with lit.[21] Benzocoumarin (6*H*-benzo[c]chromen-6-one, **5**) was prepared by oxidation of biphenyl-2-carboxylic acid with CrO_3. Colourless crystals, m.p. 92 °C (MeOH), lit.[22,23]: 92.5–93.5 °C. Thiolo-benzocumarin (6*H*-benzo[c]thiochromen-6-one, **6**) was obtained by oxidation of **8** with $Hg(OAc)_2$. Yellow needles, m.p. 125–127 °C (petroleum ether), lit.[24,25]: 130–131 °C. Thiono-benzocoumarin (6*H*-benzo[c]chromene-6-thione, **7**) was prepared by thionation of **5** with Lawesson's reagent[17,18,23] in toluene. Yellow crystals, m.p. 148–149 °C (EtOH), lit.[23]: 150–151 °C, lit.[26]: 148–150 °C. Dithio-benzocoumarin (6*H*-benzo[*c*]thiochromene-6-thione, **8**) was prepared by reaction of biphenyl-2-thiol[27] with $CSCl_2$, and subsequent intramolecular Friedel–Crafts-acylation of the intermediate biphenyl-2-yl chlorodithioformate [94%, orange oil, $C_{13}H_9ClS_2$ (264.80), Calcd C 58.97, H 3.43, Cl 13.39 S 24.22; found C 59.05, H 3.35, Cl 13.31, S 24.19] with $AlCl_3$. Red needles, m.p. 106 °C (petroleum ether), lit.[25]: 113–114 °C, lit.[28]: 106 °C.

The polarographic and cyclovoltammetric measurements, the generation of the radical anions by *in situ* electroreduction in DMF at room temperature, and the recording of the EPR spectra were performed as described previously.[2] The *g*-factors were determined by direct measurement of the field H_o and the microwave frequency ν_o according to $g = 7.14484\cdot10^{-11}\ \nu_o\cdot H_o^{-1}$ and corrected by using the perylene radical cation (g = 2.002569) as internal standard. Spectra simulations were carried out by using the SIMFONIA program (Bruker).

Simple HMO calculations were performed by use of the online program SHMO.[29] An unpublished FORTRAN-77 program HUECKEL[30,31] was used for the McLachlan type calculations. The applied Coulomb and resonance parameters are compiled in Table 4. They differ slightly from the literature data for open-chain benzoates (**1** and **5**),[32] thiolobenzoates (**2** and **6**),[6] thionobenzoates (**3** and **7**)[5] and dithiobenzoates (**4** and **8**);[5] see above.

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