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EPR Studies on Carboxylic Esters. Part 15.[1] Spin Density Distribution in the Radical Anions of Naphthalenecarboxylic Esters

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The spin density distribution in the radical anions of naphthalene-mono-, di- and -tetra-carboxylic esters is determined from the proton hfs coupling constants as measured by EPR spectroscopy and discussed in terms of semi-empirical MO calculations.

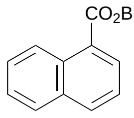
In 1993 Y. Kubo *et al.*[2] reported on the spin density distribution in selected dimethyl naphthalenedicarboxylate radical anions. These species were discussed as intermediates in photoallylation reactions of the esters. Although the authors determined the spin densities theoretically, they did not perform experimental measurements. Since we have been engaged for many years in the investigation of spin density distributions of ester[3] and thioester[1,4] radical anions, we were interested in the question of whether the alkyl naphthalenecarboxylate radical anions postulated by the Japanese group were persistent enough to be studied by EPR spectroscopy. Furthermore, we wanted to verify and corroborate the theoretical data by exploitation of the proton hfs coupling constants using McConnell's relation.

To our knowledge no EPR spectroscopic results on naphthoic esters had been previously published, whereas the radical anions of naphthalene and alkylnaphthalenes have been well known for several decades.[5] We have therefore studied the diesters dealt with in Kubo's publication and in addition the corresponding mono- as well as several further oligo-esters.

In situ electroreduction of **1**–**11** in dry DMF achieved the corresponding radical anions. Their EPR spectra were well resolved in most cases. Complete sets of proton hyperfine coupling constants were derived from the spectra and were verified by spectrum simulation. The *g*-factors ranged between 2.0032 and 2.0035.

The assignment of the coupling constants a_μ^H to specific positions was not straightforward in any of the cases. The alkyl proton couplings were unequivocal because of their multiplicity. Ring protons were identified from the symmetry of the molecule or, if possible, from changes in the spectra after introduction of *tert*-butyl substituents.

On the other hand, the theoretical spin densities ρ_μ^π were quoted to determine and assign a_μ^H from McConnell's relation $a_\mu^H = -2.7\rho_\mu^\pi$. Neither HMO nor AM1 calculations led to a perfect agreement between the experimental and theoretical data (see Table 4). However, the sequence of at least the more important large coupling constants was reproduced satisfactorily. Since the AM1 spin densities came out slightly better than the HMO results in most cases and, moreover, are more convincing from a theoretical point of view, we preferred the former for the assignments. The results are compiled in Table 1.



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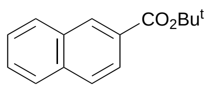

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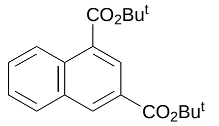

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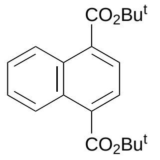

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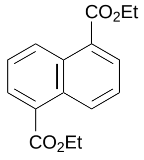

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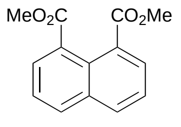

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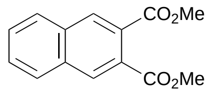

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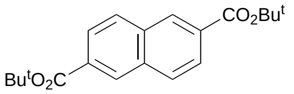

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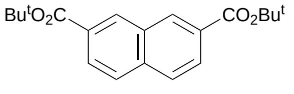

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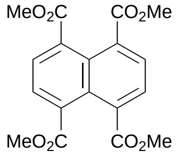

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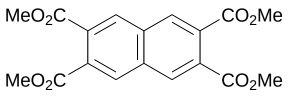

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As one would expect, the spin densities and thus the proton hfs coupling constants in the naphthoate radical

Table 1 Proton hfs coupling constants a_μ^H (mT) in the alkyl naphthalenecarboxylate radical anions $\mathbf{1}^{\bullet-}$–$\mathbf{11}^{\bullet-}$

Ester	a_1^H	a_2^H	a_3^H	a_4^H	a_5^H	a_6^H	a_7^H	a_8^H	a_R^H
1	—	0.482	0.083	0.760	0.0	0.025	0.229	0.266	—
2	0.637	—	0.022	0.178	0.085	0.412	0.044	0.366	—
3	—	0.033	—	0.867	0.362	0.066	0.346	0.133	—
4	—	0.203	0.203	—	0.105	0.078	0.078	0.105	—
5	—	0.129	0.238	0.406	—	0.129	0.238	0.406	0.033 (4 H)
6	—	0.371	0.0	0.542	0.542	0.0	0.371	—	0.034 (6 H)
7	0.260	—	—	0.260	0.130	0.130	0.130	0.130	0.025 (6 H)
8	0.307	—	0.066	0.250	0.307	—	0.066	0.250	—
9	0.693	—	0.140	0.140	0.140	0.140	—	0.693	—
10	—	0.158	0.158	—	—	0.158	0.158	—	0.030 (12 H)
11	0.250	—	—	0.250	0.250	—	—	0.250	0.026 (12 H)

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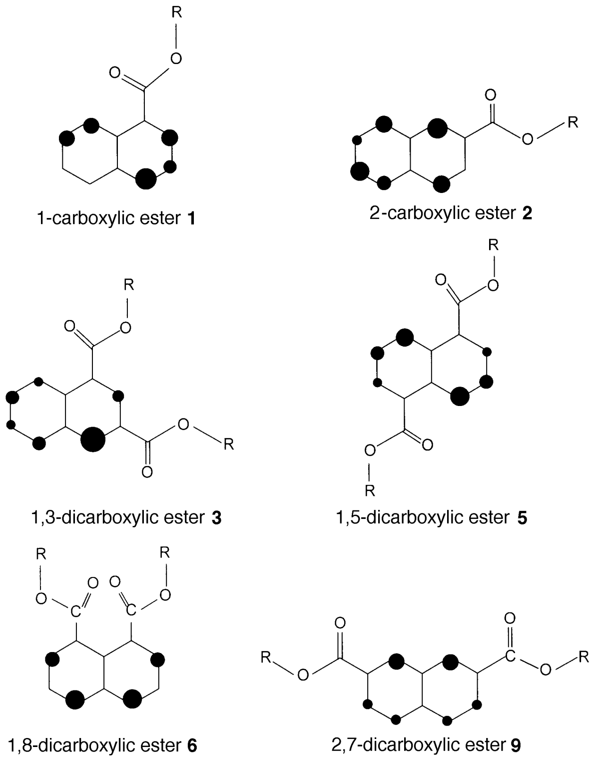
Table 4 Comparison of experimental [$\rho^{\pi}_{\mathrm{exp}}=a^{\mathrm{H}}_{\mu}$ (mT)/ − 2.7 (mT)] and theoretical spin densities ρ^{π}_{μ} in $\mathbf{1}^{\bullet-}$–$\mathbf{4}^{\bullet-}$, $\mathbf{7}^{\bullet-}$ and $\mathbf{8}^{\bullet-}$

		Centre μ of the naphthalene system							
Comp.	Method	1	2	3	4	5	6	7	8
$\mathbf{1}^{\bullet-}$	Exp	—	0.179	0.031	0.282	0	0.009	0.085	0.096
	AM1	—	0.160	0.006	0.203	0.009	0.035	0.076	0.084
	MNDO	—	0.156	0.081	0.225	0.081	0.042	0.092	0.022
	HMO	—	0.150	0.024	0.202	0.085	0.018	0.057	0.053
$\mathbf{2}^{\bullet-}$	Exp	0.236	—	0.008	0.066	0.031	0.153	0.016	0.136
	AM1	0.154	—	0.003	0.086	0.019	0.139	0.003	0.136
	MNDO	0.210	—	0.026	0.072	0.065	0.103	0.046	0.066
	HMO	0.243	—	0.006	0.062	0.049	0.084	0.008	0.109
$\mathbf{3}^{\bullet-}$	Exp	—	0.012	—	0.321	0.134	0.024	0.128	0.049
	AM1	—	0.000	—	0.245	0.138	0.036	0.117	0.063
	MNDO	—	0.002	—	0.237	0.143	0.004	0.145	0.062
	HMO	—	0.055	—	0.284	0.086	0.005	0.076	0.019
$\mathbf{4}^{\bullet-}$	Exp	—	0.075	0.075	—	0.039	0.029	0.029	0.039
	AM1	—	0.090	0.090	—	0.054	0.035	0.035	0.054
	MNDO	—	0.086	0.086	—	0.109	0.051	0.051	0.109
	HMO	—	0.083	0.083	—	0.041	0.015	0.015	0.041
$\mathbf{7}^{\bullet-}$	Exp	0.096	—	—	0.096	0.048	0.048	0.048	0.048
	AM1	0.076	—	—	0.076	0.056	0.043	0.043	0.056
	MNDO	0.210	—	—	0.210	0.009	0.059	0.059	0.009
	HMO	0.051	—	—	0.051	0.010	0.028	0.028	0.010
$\mathbf{8}^{\bullet-}$	Exp	0.114	—	0.024	0.093	0.114	—	0.024	0.093
	AM1	0.117	—	0.059	0.080	0.117	—	0.059	0.080
	MNDO	0.112	—	0.006	0.084	0.112	—	0.006	0.084
	HMO	0.169	—	0.005	0.066	0.169	—	0.005	0.066

anions are larger in the ester-substituted moiety of the naphthalene system (*cf*. Fig.). Especially the α-naphthoate ester resembles the benzoate ester[6] in so far as 4-H and 2-H exhibit the largest coupling constants. In the β-series a similarity of the spin density distribution with the unsubstituted naphthalene radical anion[5] is recognized. This effect is due to the less pronounced perturbation of the LUMO by an electron-withdrawing ester substituent in a position (β) with a smaller orbital coefficient. The spin density distribution in the di- and tetra-ester radical anions corresponds well to the expectations and the observations in the monoester series.



1-carboxylic ester **1**

2-carboxylic ester **2**

1,3-dicarboxylic ester **3**

1,5-dicarboxylic ester **5**

1,8-dicarboxylic ester **6**

2,7-dicarboxylic ester **9**

Fig. Graphical representation of the spin density distribution (area of circles proportional to a^{H}_{μ}) in $\mathbf{1}^{\bullet-}$, $\mathbf{2}^{\bullet-}$, $\mathbf{3}^{\bullet-}$, $\mathbf{5}^{\bullet-}$, $\mathbf{6}^{\bullet-}$, $\mathbf{9}^{\bullet-}$

Especially in $\mathbf{5}^{\bullet-}$, $\mathbf{6}^{\bullet-}$ and $\mathbf{9}^{\bullet-}$ the total spin density distribution appears as a double image of the ester moieties of $\mathbf{1}^{\bullet-}$ or $\mathbf{2}^{\bullet-}$, respectively. The asymmetric diester **3** seems, however, to represent an interesting exceptional case. Only 4-H, and to a lesser extent 5-H and 7-H, exhibit high spin densities, but 2-H does not. The four ester groups in $\mathbf{10}^{\bullet-}$ and $\mathbf{11}^{\bullet-}$ obviously remove most of the spin density from the naphthalene ring (see Table 1).

As mentioned, Kubo *et al.*[2] have calculated spin densities in several dimethyl naphthalenedicarboxylate radical anions ($\mathbf{3}^{\bullet-}$, $\mathbf{4}^{\bullet-}$, $\mathbf{7}^{\bullet-}$, $\mathbf{8}^{\bullet-}$). These workers applied the MNDO method and, using our own method, we have confirmed exactly their results. However, the MNDO data do not agree well with the experimental data in any case (*cf.* Table 4).

Techniques used: ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, mass spectroscopy, differential pulse polarography, cyclic voltammetry, EPR spectroscopy, MO calculations

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References cited in this synopsis

1 Part 14. J. Voss, T. Behrens, M. Krasmann, K. Osternack and L. Prangova, *J. Chem. Res.* (*S*), 1997, 252.

2 Y. Kubo, T. Todani, T. Inoue, H. Ando and T. Fujiwara, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 541.

3 J. Voss, *Tetrahedron*, 1971, **27**, 3753.

4 (*a*) J. Voss and K. Schlapkohl, *Tetrahedron*, 1975, **31**, 2982; (*b*) J. Voss, W. Schmüser and K. Schlapkohl, *J. Chem. Res.*, 1977, (*S*) 144; (*M*) 1801; (*c*) U. Debacher, W. Schmüser and J. Voss, *J. Chem. Res.*, 1982, (*S*) 74; (*M*) 0876; (*d*) J. Gassmann, H. Günther, K. Osternack, A. Sawluk, K. Thimm and J. Voss, *Magn. Reson. Chem.*, 1994, **32**, 624.

5 F. Gerson, B. Weidmann and E. Heilbronner, *Helv. Chim. Acta*, 1964, **47**, 1951.

6 M. Hirayama, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 1822.