194. The Radical Cations and the Radical Anions of Some *Weitz*-Type S-Donors

by **Fabian Gerson***, **Georg Gescheidt**, and **Jürgen Knöbel**[1])

Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

and **Ichiro Murata** and **Kazuhiro Nakasuji**

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

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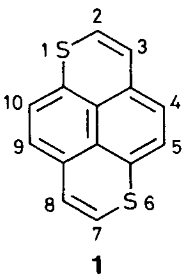
The radical cations and the radical anions of 1,6-dithiapyrene (**1**) and 3,10-dithiaperylene (**2**) as well as those of three further *Weitz*-type S-donors **3**, **4**, and **5** have been studied by ESR spectroscopy. The experimental findings for **1**$^{\cdot-}$ (widths and behaviour on saturation of hyperfine lines) suggest that the ground state of this radical anion is effectively degenerate. With the exception of **1**$^{\cdot-}$, the ESR studies of all radical ions could be complemented by the use of the ENDOR and general TRIPLE resonance techniques. In addition to proton hyperfine data, ^{33}S coupling constants have been determined for **1**$^{\cdot+}$ (0.53 mT), **2**$^{\cdot+}$ (0.46 mT), and **4**$^{\cdot+}$ (0.34 mT); they are in agreement with the predicted substantial π-spin populations at the S-atoms.

Introduction. – The search for electron donors as components of molecular conductors ('organic metals') has stimulated the syntheses of new S-containing, electron-rich π-systems [1] [2]. Among others, several *Weitz*-type [3] donors have been prepared in which two S-atoms are incorporated *i)* in a C-framework of a polycyclic aromatic compound or *ii)* in two arylidene moieties linked by a =C=C= cumulene unit. Here, the class *(i)* consists of 1,6-dithiapyrene (**1**) [4], 3,10-dithiaperylene **2** [4], and 5,13-dithiaaceanthryleno[2,1-*a*]aceanthrylene (**3**) [5], while the class *(ii)* is represented by 4,4′-(1,2-ethenediylidene)bis[2,6-diphenyl-4*H*-thiopyran] (**4**) [6] and 9,9′-(1,2-ethenediylidene)bis-9*H*-thioxanthene (**5**) [7].



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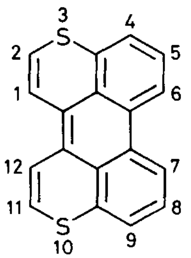

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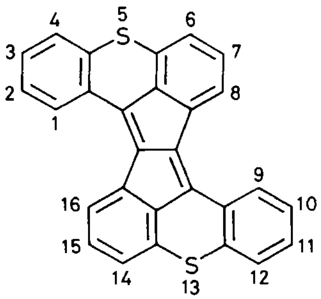

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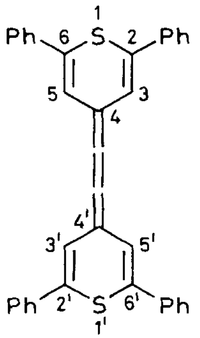
[1]) Present address: *F. Hoffmann-La Roche & Co. AG*, CH-4002 Basel.



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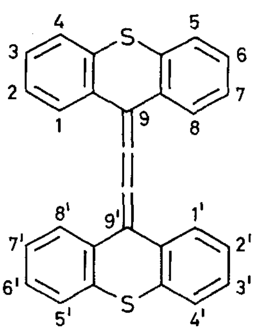

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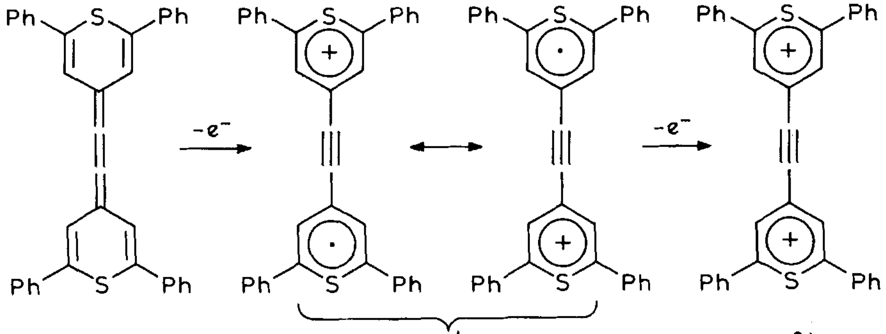
The compounds **1**, **2**, **4**, and **5** are known to convert readily into the dications [4] [6–8], with the radical cations occurring as intermediates, *e.g.*:



Although formation of the dication has not been observed for **3**, conversion to the radical cation is indicated by electrochemical studies [5]. It will be shown in the present paper that the electron donors **1**–**5** can be reduced to the radical anions by reaction with an alkali metal or by electrolysis. Both the radical cations, $\mathbf{1}^{+\cdot}$–$\mathbf{5}^{+\cdot}$, and the radical anions, $\mathbf{1}^{-\cdot}$–$\mathbf{5}^{-\cdot}$, are characterized by their g-factors and hyperfine data with the use of ESR, ENDOR, and TRIPLE resonance spectroscopy.

Experimental. – The compounds **1**–**5** have been synthesized as described previously [4–7]. Upon oxidation with $AlCl_3$ or $CF_3COOH/(CF_3CO)_2O$ (2:1) in CH_2Cl_2, they easily yielded very persistent radical cations, $\mathbf{1}^{+\cdot}$–$\mathbf{5}^{+\cdot}$. The radical anions, $\mathbf{1}^{-\cdot}$–$\mathbf{5}^{-\cdot}$, were obtained by reaction of **1**–**5** with K or Cs in 1,2-dimethoxyethane (DME) or by electrolytic reduction in this solvent (supporting salt Bu_4NClO_4); their persistence was considerably lower than that of the corresponding cations. For the electrolysis, it proved advantageous not to amalgamate the helical Au cathode, as it had been done in previous work involving hydrocarbons [9] [10]. The half-wave reduction potentials, $E_{1/2}^{red}$, of **1** and **2** were measured at 298 K by cyclic voltammetry with MeCN as the solvent (supporting salt Et_4NClO_4); in the case of **3**, **4**, and **5**, which are almost insoluble in MeCN, this solvent was replaced by CH_2Cl_2 (supporting salt Bu_4NClO_4). A hanging Hg drop electrode (*VA*-Stand *663 Metrohm*) served as the working electrode. The scan rate was 400 mV/s. The ESR, ENDOR, and TRIPLE resonance studies were conducted at 213–273 and 183–213 K for the radical cations and anions, respectively. The apparatus was a *Varian-E9* instrument for ESR and a *Bruker-ESP-300* spectrometer system for ENDOR and TRIPLE resonance.

Table 1. *Half-Wave Oxidation and Reduction Potentials,* $E^{ox}_{1/2}$ *and* $E^{red}_{1/2}$ [V *vs.* SCE] *of* **1**–**5**

	1	**2**	**3**	**4**	**5**
$E^{ox(1)}_{1/2}$	+0.36 [4]	+0.42 [4]	+0.72 [5]	+0.14 [6]	+0.65 [8][a])
$E^{ox(2)}_{1/2}$	+0.75 [4]	+0.76 [4]	[b])	+0.49 [6]	+0.81 [8][a])
$E^{red(1)}_{1/2}$	−2.30[c])	−1.87[c])	−0.95[c])	−1.44[c])	−1.15[c])

[a]) Modified relative to the values given previously in [7]. [b]) Not observed [5]. [c]) ±0.05 V; for conditions, see *Experimental.*

Table 2. *Coupling Constants,* a_{H_μ} [mT], *of the Protons in Positions* μ, *Total Widths,* t.w. [mT], *of the ESR Spectra and g-Factors for the Radical Ions of* **1**–**5**[a])

	$\mathbf{1}^{\cdot+}$	$\mathbf{1}^{\cdot-}$	μ
a_{H_μ}	−0.184	(−)0.270[b])	2,7 (2H)
	−0.126	(−)0.247[b])	3,8 (2H)
	−0.166	(−)0.082[b])	4,9 (2H)
	−0.126	(+)0.008[b])	5,10 (2H)
t.w.	1.20	1.21	
g	2.0057	2.0035	

	$\mathbf{2}^{\cdot+}$	$\mathbf{2}^{\cdot-}$	μ
a_{H_μ}	−0.086	+0.127	1,12 (2H)
	−0.247	−0.410	2,11 (2H)
	−0.073	+0.040	4,9 (2H)
	−0.030	−0.172	5,8 (2H)
	−0.086	+0.027	6,7 (2H)
t.w.	1.04	1.55	
g	2.0055	2.0037	

	$\mathbf{3}^{\cdot+}$	$\mathbf{3}^{\cdot-}$	μ
a_{H_μ}	−0.043	−0.199	1,9 (2H)
	−0.043	+0.059	2,10 (2H)
	−0.067	−0.144	3,11 (2H)
	(+)0.004[b])	+0.041	4,12 (2H)
	−0.101	−0.049	6,14 (2H)
	−0.018	−0.181	7,15 (2H)
	−0.198	−0.005	8,16 (2H)
t.w.	0.95	1.36	
g	2.0050	2.0030	

	$\mathbf{4}^{\cdot+}$	$\mathbf{4}^{\cdot-}$	μ
a_{H_μ}	−0.023	+0.109	3,3′, 5,5′ (4H)
	−0.032	−0.076	Ph-*ortho* (8H)
	+0.015	+0.026	Ph-*meta* (8H)
	−0.032	−0.087	Ph-*para* (4H)
t.w.	0.60	1.60	
g	2.0048	2.0038	

	$\mathbf{5}^{\cdot+}$	$\mathbf{5}^{\cdot-}$	μ
a_{H_μ}	−0.064	−0.177	1,1′, 8,8′ (4H)
	+0.023	+0.055	2,2′, 7,7′ (4H)
	−0.117	−0.171	3,3′, 6,6′ (4H)
	−0.005	+0.031	4,4′, 5,5′ (4H)
t.w.	0.84	1.74	
g	2.0045	2.0030	

[a]) Experimental error: ±0.001 mT in the coupling constants and ±0.0001 in the g-factors.

[b]) Sign indicated by MO model without information from TRIPLE resonance.

Results. – *Table 1* lists the half-wave oxidation potentials, $E^{ox(1)}_{1/2}$ and $E^{ox(2)}_{\frac{1}{2}}$ [4–8], along with the corresponding $E^{red(1)}_{1/2}$ values determined in the present work.

The proton coupling constants, a_{H_μ}, and g-factors of $\mathbf{1}^{\cdot+}$–$\mathbf{5}^{\cdot+}$ and $\mathbf{1}^{\cdot-}$–$\mathbf{5}^{\cdot-}$ are compiled in *Table 2*. Except for $\mathbf{1}^{\cdot-}$ (*cf.* the end of the section), high resolution was achieved in the ESR spectra of all radical ions. This is impressively demonstrated in *Fig. 1* by the spectrum of $\mathbf{5}^{\cdot+}$, in which the hyperfine splitting of 0.005 mT from four equivalent protons has been completely resolved.

Analyses of the ESR spectra were facilitated and secured by the use of the ENDOR technique which was successfully applied to $\mathbf{1}^{\cdot+}$–$\mathbf{5}^{\cdot+}$ and $\mathbf{2}^{\cdot-}$–$\mathbf{5}^{\cdot-}$, *i.e.*, again with the notable exception of $\mathbf{1}^{\cdot-}$. The proton ENDOR spectra of $\mathbf{3}^{\cdot+}$ and $\mathbf{3}^{\cdot-}$, shown in the upper part of *Fig. 2*, are chosen as illustrative examples, since these radical ions represent here paramagnetic species with the highest number of different coupling constants a_{H_μ}. The

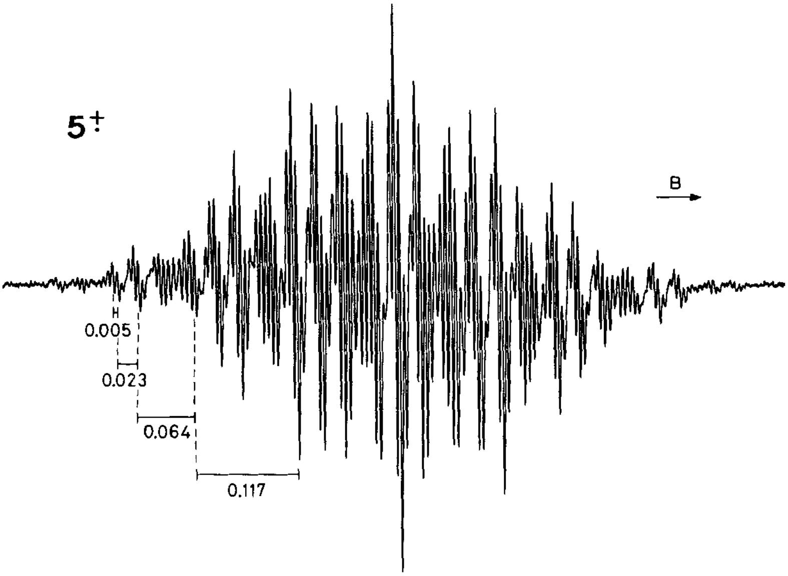


Fig. 1. *ESR spectrum of* 5^{+}. Solvent: CH_2Cl_2; temp. 273 K. The coupling constants are indicated in mT.

larger widths of the ENDOR signals for the cation, as compared to those for the anion, were likewise encountered with the remaining radical ions amenable to the ENDOR technique in this series.

The radical ions $\mathbf{1}^{+}$–$\mathbf{5}^{+}$ and $\mathbf{2}^{-}$–$\mathbf{5}^{-}$ were also studied by general TRIPLE resonance, so that relative signs could be allotted to the coupling constants a_{H_μ}, according to well-known criterions [11]. The TRIPLE resonance spectra are exemplified in the lower part of *Fig. 2* by those of $\mathbf{3}^{+}$ and $\mathbf{3}^{-}$. In the case of $\mathbf{3}^{+}$, the *same* sign is required for the coupling constants of 0.198, 0.101, 0.067, 0.043, and 0.018 mT; as for $\mathbf{3}^{-}$, the a_{H_μ} values of 0.199, 0.181, 0.144, 0.049, and 0.005 mT should have the *same* sign which is *opposite* to that of 0.059 and 0.041 mT.

The information thus provided by the TRIPLE resonance technique has been combined with the results of the HMO-*McLachlan*-type calculations [12] in which use was made of the well-tried heteroatom parameters $\alpha_S = \alpha + \beta$ and $\beta_{CS} = 0.7\beta$ [13]. The resulting absolute signs of the coupling constants a_{H_μ} and the assignments of these values to the sets of equivalent protons in the individual positions μ are indicated in *Table 2*. It is obvious that the assignments are less certain, when two or more coupling constants have a similar magnitude and the same sign.

Coupling constants, a_S, of naturally abundant ^{33}S isotopes were measured for $\mathbf{1}^{+}$, $\mathbf{2}^{+}$, and $\mathbf{4}^{+}$. *Fig. 3* illustrates the procedure by presenting the ESR spectrum of $\mathbf{1}^{+}$ flanked by the peripheral ^{33}S satellite lines. The coupling constant a_S associated with these lines is 0.530 ± 0.005 mT; the analogous values for $\mathbf{2}^{+}$ and $\mathbf{4}^{+}$ are 0.46 ± 0.01 and 0.34 ± 0.01 mT, respectively. It is noteworthy that the ^{33}S satellite lines at the low-field end of the ESR spectra have higher amplitudes, *i.e.* they are narrower than their counterparts at the high-field end. Since the π-spin populations, ρ_S, at the S-atoms in $\mathbf{1}^{+}$, $\mathbf{2}^{+}$, and $\mathbf{4}^{+}$ are

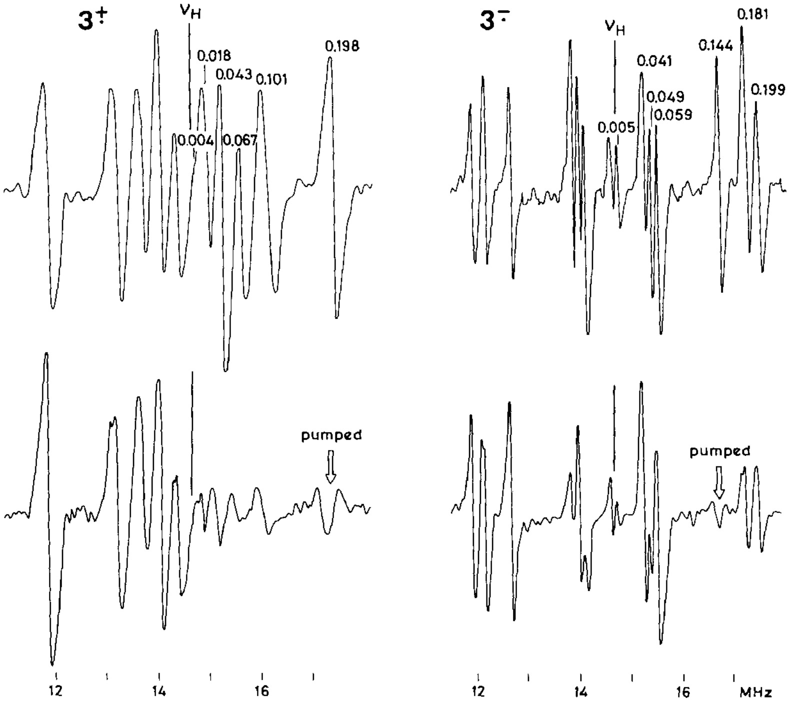


Fig. 2. *Proton ENDOR* (top) *and general TRIPLE resonance spectra* (bottom) *of* **3**$^{+}$ *and* **3**$^{-}$. Solvent: CH_2Cl_2 (**3**$^{+}$) and DME (**3**$^{-}$; counterion: K^+); temp.: 233 (**3**$^{+}$) and 193 K (**3**$^{-}$). The numbers [mT] refer to the coupling constants associated with the ENDOR signals. Except for 0.043 mT which is assigned to *two* pairs of protons in **3**$^{-}$ (accidental equivalence), all these values are due to two protons.

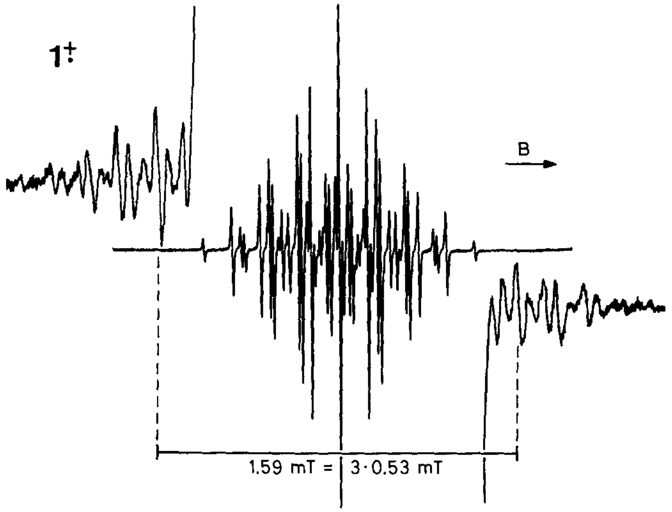


Fig. 3. *ESR spectrum of* **1**$^{+}$ *showing* ^{33}S *satellite lines* (recorded at higher amplification and larger modulation amplitude). Solvent: CH_2Cl_2; temp. 253 K.

predicted to be positive *(cf. Discussion)*, this behaviour bears out the expectation that the sign of the coupling constants a_S is positive as well [14].

As stated above, some features of **1**$^{-\cdot}$ distinguished it from other radical ions in the series. This statement is based on the following findings: *i)* The hyperfine lines in the ESR spectrum of **1**$^{-\cdot}$ were wider by an order of magnitude than those observed for the remaining radical ions. Moreover, the poor resolution of this spectrum could not be improved by changes in experimental conditions such as dilution, variations of temperature, and replacement of the counterion K^+ by Cs^+ or Bu_4N^+. *ii)* Using the available spectroscopic apparatus *(cf. Experimental)*, it was not possible to saturate the ESR lines, so that ENDOR and TRIPLE resonance spectra of **1**$^{-\cdot}$ were not obtained. *iii)* The agreement between the observed and calculated proton coupling constants was significantly worse than for **1**$^{+\cdot}$–**5**$^{+\cdot}$ and **2**$^{-\cdot}$–**5**$^{-\cdot}$. The structural peculiarity responsible for these findings will be considered below.

Discussion. – Each of the two S-atoms which bestow the pronounced donor properties upon the compounds **1**–**5**, contributes an electron pair to the π system. As a consequence, these compounds contain two more π electrons than the corresponding conjugated hydrocarbons, so that, in general, the HOMO and the LUMO of the former correlate with the LUMO and the NLUMO of the latter, respectively (NLUMO = Next Lowest Unoccupied MO). Such correlation is schematically depicted in *Fig. 4* for **2** and its hydrocarbon analogue, perylene. Since the dithia substitution stabilizes both relevant orbitals, the perylene NLUMO (which becomes the LUMO of **2**) is shifted into a region

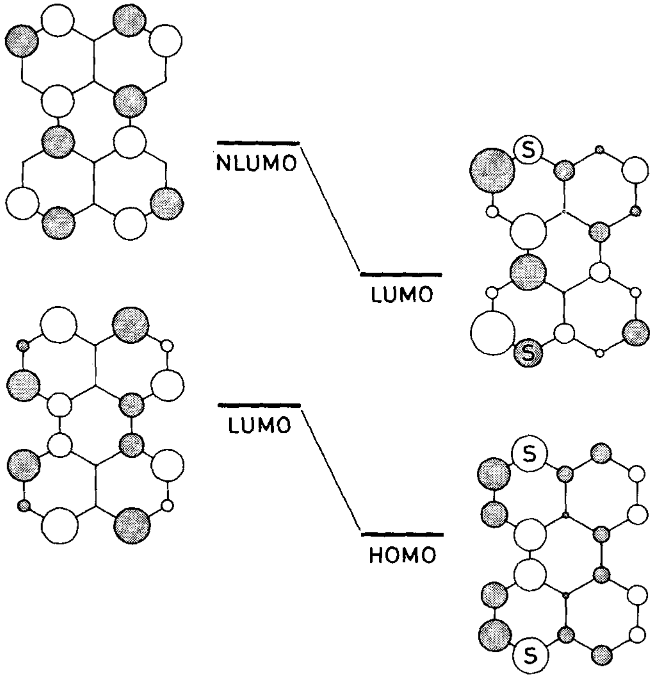


Fig. 4. *Diagram correlating the frontier orbitals of* **2** (right) *with the LUMO and NLUMO of perylene* (left). Heteroatom parameters: $\alpha_S = \alpha + \beta$; $\beta_{CS} = 0.7\beta$ (*cf.* text).

of lower energy appropriate for the uptake of an additional electron. Actually, the half-wave reduction potentials, $E_{1/2}^{\text{red}(1)}$, of **1** (–2.30 V) and **2** (–1.87 V) are only 0.2 V more negative than those of their hydrocarbon analogues pyrene (–2.11 V) and perylene (–1.67 V) [15]. In general, the experimental potentials $E_{1/2}^{\text{red}(1)}$ of **1**–**5** *(Table 1)* appear to be less negative than the values predicted by their relation with the LUMO energies [9] [15], when these are calculated by the use of parameters $\alpha_S = \alpha + \beta$ and $\beta_{CS} = 0.7\beta$.

The radical anion **1**$^{\cdot -}$ represents an exceptional case in that the correlation of the LUMO of **1** with a π orbital of pyrene is less straightforward than for **2**–**5** and the corresponding hydrocarbons. This is because the NLUMO of pyrene should only be slightly stabilized by the introduction of the two S-atoms at the 1,6-positions, whereas a higher-lying MO is expected to be markedly lowered in energy by such a substitution. As a result, the two MO's, belonging to different representations (A_u and B_g) of C_{2h}, are predicted to be energetically close enough to compete for the LUMO of **1**. In fact, experimental findings strongly suggest that these MO's are effectively equal in energy. Since orbital degeneracy can shorten the electron spin-lattice relaxation time [16], it would account both for the observed broadening of the hyperfine lines in the ESR spectrum of **1**$^{\cdot -}$ and for the failure to saturate them. Also, the unsatisfactory agreement between theory and experiment in the case of **1**$^{\cdot -}$ may be traced to an inadequate treatment of the π-spin distribution in terms of the unpaired electron occupying a single non-degenerate orbital [17].

Characteristic of all radical ions **1**$^{\cdot +}$–**5**$^{\cdot +}$ and **1**$^{\cdot -}$–**5**$^{\cdot -}$ is the small total width of their ESR spectra which amounts merely to 0.6–1.2 mT for the cations and to 1.2–1.7 mT for the anions *(Table 2)*. This spectral feature is rationalized by the substantial π-spin populations at the S-atoms and the 'blind' C-centres which, being void of protons, do not contribute to the hyperfine pattern of the main ESR spectrum. The finding that the total width is mostly smaller for the radical cations than for the corresponding anions is consistent with the higher π-spin populations, ρ_S, at the S-atoms in the former relative to the latter ions. A direct experimental test of the calculated ρ_S values is provided by the ^{33}S coupling constants, a_S, observed for **1**$^{\cdot +}$, **2**$^{\cdot +}$, and **4**$^{\cdot +}$. As can be gathered from *Table 3*, the relationship $a_S = Q_S\rho_S$ is obeyed, and the proportionality factor Q_S resulting therefrom (+3.4 to +3.5 mT) differs only slightly from that reported in the literature (+3.3 mT [13] [14] [18]). The expected dependence of the g-factors on the ρ_S values [19] is likewise apparent *(Table 3)*. The substantial π-spin populations ρ_S in **1**$^{\cdot +}$–**5**$^{\cdot +}$ indicate a marked enhancement of the positive charge at the S-atoms on passing from the neutral compounds to the corresponding radical cations. The propensity of these atoms to accept such a charge is in accord with their dominant contribution to the donor properties of **1**–**5**.

Table 3. *Calculated π-Spin Populations ρ_S* [a]) *in the Radical Ions of* **1**–**5** vs. *Observed Coupling Constants a_S* [mT] *and g-Factors*

	1$^{\cdot +}$	**2**$^{\cdot +}$	**3**$^{\cdot +}$	**4**$^{\cdot +}$	**5**$^{\cdot +}$	**1**$^{\cdot -}$	**2**$^{\cdot -}$	**3**$^{\cdot -}$	**4**$^{\cdot -}$	**5**$^{\cdot -}$
ρ_S	+0.154	+0.130	+0.116	+0.099	+0.087	+0.046[b])	+0.066	+0.038	+0.078	+0.025
a_S	+0.530	+0.46	–	+0.34	–	–	–	–	–	–
g	2.0057	2.0055	2.0050	2.0048	2.0045	2.0035	2.0037	2.0030	2.0038	2.0030

[a]) HMO-*McLachlan* procedure: $\alpha_S = \alpha + \beta$; $\beta_{CS} = 0.7\beta$; $\lambda = 1.2$ (*cf.* text).

[b]) Averaged over the single occupancy of two effectively degenerate MO's (*cf.* text).

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