

225. The Radical Ions of Naphtho[1,8-*cd*]-[1,2,6]thiadiazine and Some of Its Derivatives

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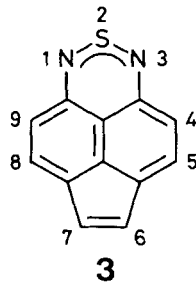
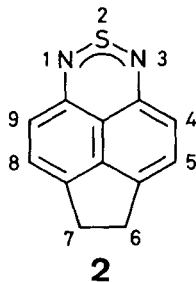
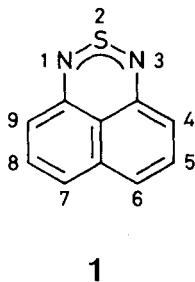
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Summary

The radical cations and anions of naphtho[1,8-*cd*]-[1,2,6]thiadiazine (**1**) and 6,7-dihydroacenaphtho[5,6-*cd*]-[1,2,6]thiadiazine (**2**), as well as the radical anion of acenaphtho[5,6-*cd*]-[1,2,6]thiadiazine (**3**) have been characterized by ESR spectroscopy. The π -spin distributions in the radical cations **1**^{•+} and **2**^{•+} strongly resemble those in the iso- π -electronic phenalenyl radical. A prominent feature of the radical anions **1**^{•-}, **2**^{•-} and **3**^{•-} is the substantial localization of the π -spin population on the thiadiazine fragment. These findings are satisfactorily accounted for by HMO models using conventional heteroatom parameters.

Introduction. - Phenalenyl radical has been the subject of numerous ESR studies (see, e.g., [1-3]). However, analogous investigations on structurally related heterocycles, such as the radical cation of cycl[3.3.3]azine [4], are rather scarce. Since naphtho[1,8-*cd*]-[1,2,6]thiadiazine (**1**) is iso- π -electronic with the phenalenyl anion (**4**^{•-}), the radical cation **1**^{•+} and the radical anion **1**^{•-} are iso- π -electronic with the phenalenyl radical (**4**[•]) and radical dianion (**4**^{•-}), respectively. The ionization energy of **1** in the gas phase (7.64 eV, as determined by PE. spectroscopy [5]) is sufficiently low to warrant thermodynamic stability of **1**^{•+} in solution. Also, due to the presence of the three heteroatoms, the electron affinity of **1** is rather high



(half-wave reduction potential -0.96 V [6]), so that $1^{\oplus}$ can readily be generated by standard procedures. In this respect, it is noteworthy that the iso- π -electronic counterpart of $1^{\oplus}$, the radical dianion $4^{\ominus}$, has not yet been prepared.

The present paper describes the ESR. spectra of the radical ions of naphtho[1,8-*cd*]-[1,2,6]thiadiazine (**1**) and 6,7-dihydroacenaphtho[5,6-*cd*]-[1,2,6]thiadiazine (**2**). The radical anion of acenaphtho[5,6-*cd*]-[1,2,6]thiadiazine (**3**) is also investigated.

To our knowledge, only the radical anion of the thiadiazine **1** has been previously studied by ESR. spectroscopy [6]. The reported ^{14}N - and ^1H -coupling constants agree essentially with those obtained by us, but our results indicate a different assignment for two pairs of equivalent protons. Also, in addition to the ^{14}N - and ^1H -hyperfine data, the coupling constants of ^{33}S -isotopes in natural abundance are presently determined.

Results. – Radical cations. The kinetic stability (persistence) of the radical cations of the thiadiazines **1**, **2** and **3** decreased in the sequence $1^{\oplus} > 2^{\oplus} > 3^{\oplus}$. Whereas $1^{\oplus}$, generated by oxidation with AlCl_3 in methylene chloride, was relatively persistent at room temperature, preparation of $2^{\oplus}$ from **2** by the same procedure succeeded only when the solution was not allowed to warm up above 233 K. Neither reaction with AlCl_3 nor electrolytic oxidation of **3** in a variety of solvents [7] produced $3^{\oplus}$ in a detectable concentration. The lower persistence of $2^{\oplus}$ relative to $1^{\oplus}$ is presumably caused by a conversion of $2^{\oplus}$ into the short-lived radical cation $3^{\oplus}$ (through a formal loss of two H-atoms). An analogous conversion was observed for the radical anions (see below).

Figure 1 shows the ESR. spectrum of the radical cation $1^{\oplus}$. An amplification of the signals at the low- and high-field side reveals the presence of satellite lines due to the radical cations containing a ^{13}C -isotope. Analysis of these lines, which are also reproduced in Figure 1, enables one to determine three ^{13}C -coupling constants, each belonging to a pair of equivalent carbon sites.

The ESR. spectrum of $2^{\oplus}$ is displayed in Figure 2. The twice as large extension of this spectrum (6.67 mT) relative to that of $1^{\oplus}$ (3.30 mT) is the consequence of

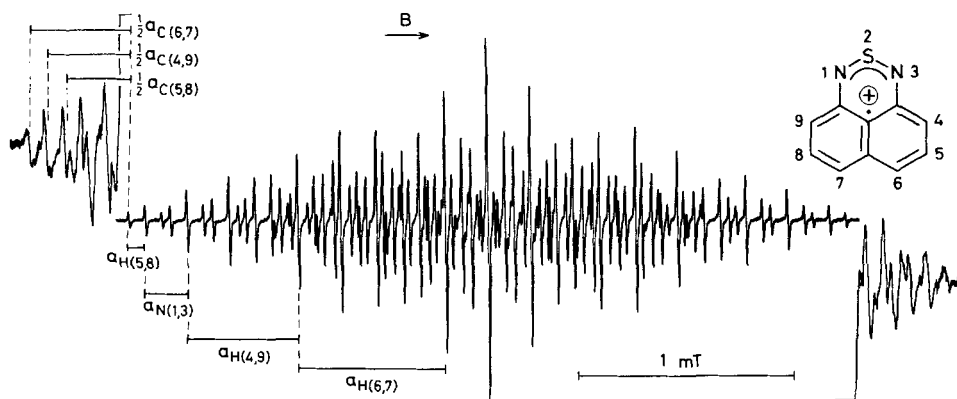


Fig. 1. ESR. spectrum of the radical cation of naphtho[1,8-*cd*]-[1,2,6]thiadiazine (**1**). Solvent CH_2Cl_2 , temperature 253 K. ^{13}C -satellite lines are displayed at both sides of the spectrum.

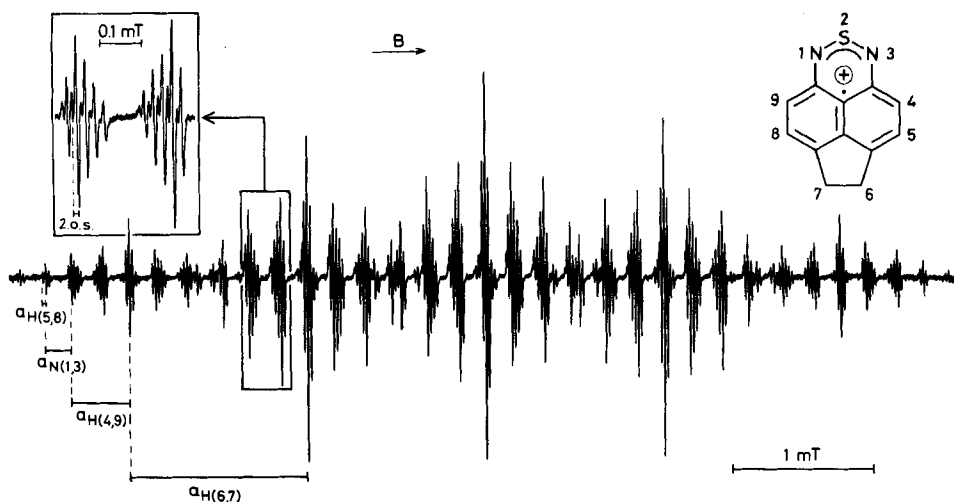


Fig. 2. ESR. spectrum of the radical cation of 6,7-dihydroacenaphtho[5,6-cd]-[1,2,6]thiadiazine (2). Solvent CH_2Cl_2 , temperature 213 K. The inset reproduces two groups of lines at an expanded scale to demonstrate the second order splitting (2.o.s.) of 0.010 mT.

replacing a coupling constant of two protons in $1^\oplus$ by a considerably larger one of four protons in $2^\oplus$. The second order splittings (0.010 mT) due to this four-proton coupling constant (1.264 mT) are resolved (Fig. 2, inset)¹⁾.

Radical anions. All three thiadiazines, 1, 2 and 3, yielded persistent radical anions upon reaction with potassium in 1,2-dimethoxyethane (DME). Electrolysis of 1, 2 and 3 in *N,N*-dimethylformamide (DMF), with tetraethylammonium perchlorate as the supporting salt, also led to persistent radical anions, provided that air was excluded. In the case of $2^\ominus$, traces of oxygen caused a rapid conversion of $2^\ominus$ into $3^\ominus$.

The ESR. spectra of $1^\ominus$, $2^\ominus$ and $3^\ominus$ are presented in Figure 3. Variations in the line-widths, which arise from *g* and ^{14}N -hyperfine anisotropies, are consistent with the positive signs of both the π -spin populations $\rho_{1,3}$ at the nitrogen centres and the ^{14}N -coupling constants $a_{\text{N}(1,3)}$. These line-widths, ΔB , can be reproduced by the use of the equation [9]

$$\Delta B = A + B M_1 + C M_1^2$$

in which $M_1 = +2, +1, 0, -1, -2$ is the quantum number of the two equivalent ^{14}N -nuclei (Fig. 3). For the parameters *A*, *B* and *C* which include the products of the *g* and/or ^{14}N -hyperfine tensors, the following values (in mT) were found adequate for $1^\ominus$ in the relatively viscous solvent DMF.

Temperature	<i>A</i>	<i>B</i>	<i>C</i>
213 K	0.010 ^{a)}	-0.005	0.004
243 K	0.009	-0.003	0.002

a) All values refer to peak-to-peak distances.

¹⁾ A further second order splitting (0.005 mT) of the same origin [8] occurs in the central part of the spectrum. It is unresolved, but affects distinctly the line-shapes.

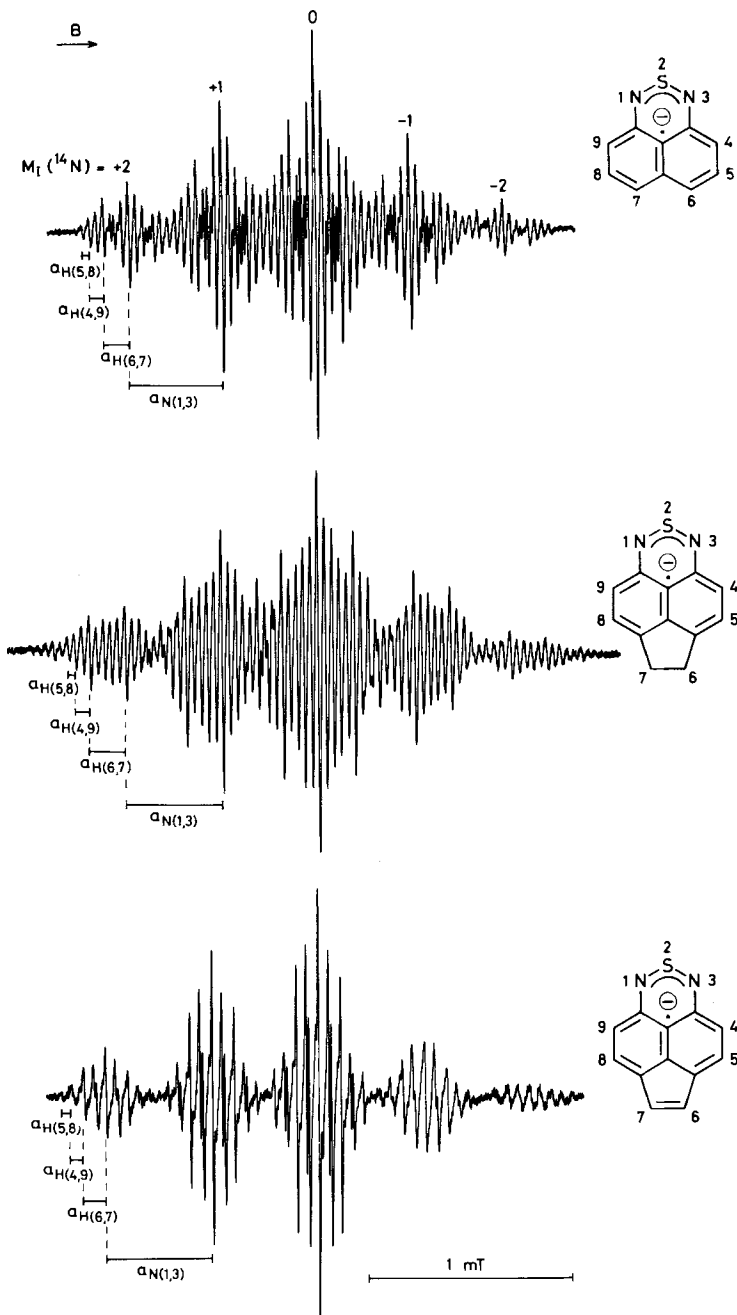


Fig. 3. ESR. spectra of the radical anions of naphtho[1,8-cd]-[1,2,6]thiadiazine (1) (top), 6,7-dihydro-acenaphtho[5,6-cd]-[1,2,6]thiadiazine (2) (middle) and acenaphtho[5,6-cd]-[1,2,6]thiadiazine (3) (bottom). Solvent DME ($1^\ominus$ and $2^\ominus$) or DMF ($3^\ominus$), counter-ion $K^\oplus$ ($1^\ominus$ and $2^\ominus$) or $Et_4N^\oplus$ ($3^\ominus$), temperature 253 K throughout.

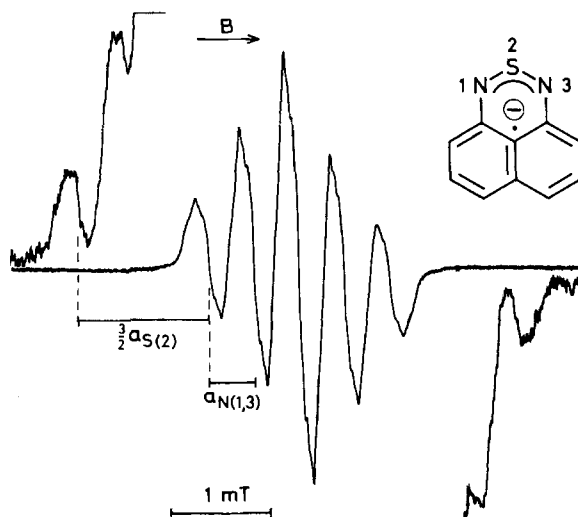


Fig. 4. ESR. spectrum of the radical anion of naphtho[1,8-cd]-[1,2,6]thiadiazine (1) showing the outermost ^{33}S -hyperfine components. Solvent DME, counter-ion K^+ , temperature 253 K.

With high radical concentrations and large modulation amplitudes, the outermost hyperfine components of the radical anions $1^\ominus$, $2^\ominus$ and $3^\ominus$ containing a ^{33}S -isotope could be detected. The larger widths of these lines at the high-field, relative to those at the low-field side, are in accord with the positive signs expected for the π -spin populations ρ_2 at the sulfur centres and for the observed ^{33}S -coupling constants. Figure 4 shows such ^{33}S -satellite lines for $1^\ominus$.

The hyperfine data and the g factors for the radical cations $1^\oplus$ and $2^\oplus$, and for the radical anions $1^\ominus$, $2^\ominus$ and $3^\ominus$ are collected in the Table. In addition to the

Table. ^{14}N -, ^1H -, ^{13}C - and ^{33}S -coupling constants, $a_{X(\mu)}$ in mT^{a)} ($X = \text{N}, \text{H}, \text{C}$ or S), and g factors^{b)} for the radical ions of naphtho[1,8-cd]-[1,2,6]thiadiazine (1), 6,7-dihydroacenaphtho[5,6-cd]-[1,2,6]thiadiazine (2) and acenaphtho[5,6-cd]-[1,2,6]thiadiazine (3)

X(μ)	Radical cations		Radical anions		
	$1^\oplus$	$2^\oplus$	$1^\ominus$	$2^\ominus$	$3^\ominus$
N(1,3)	(+)0.196	(+)0.186	+0.461 ^{c)}	+0.472 ^{c)}	+0.520 ^{c)}
H(4,9)	(-)0.508	(-)0.416	(-)0.070	(-)0.072	(-)0.062
H(5,8)	(+)0.077	(+)0.021	(+)0.035	(+)0.036	(+)0.046
H(6,7)	(-)0.674	(+)1.264 ^{d)}	(-)0.123	(+)0.175 ^{d)}	(-)0.108
C(4,9)	(+)0.75	-	-	-	-
C(5,8)	(-)0.59	-	-	-	-
C(6,7)	(+)0.93	-	-	-	-
S(2)	-	-	+0.89 ^{c)}	+0.89 ^{c)}	+0.69 ^{c)}
g	2.0027	2.0027	2.0053	2.0054	2.0054

a) Experimental error: ± 0.001 mT in $|a_{\text{H}(\mu)}| < 0.1$ mT, ± 0.002 mT in $|a_{\text{H}(\mu)}| > 0.1$ mT and in $|a_{\text{N}(1,3)}|$, ± 0.01 mT in $|a_{\text{C}(\mu)}|$ and $a_{\text{S}(2)}$. Signs as required by theory.

b) Experimental error: ± 0.0001 .

c) Sign confirmed by the studies of line-widths.

d) Four methylene protons.

coupling constants of the ^{14}N -nuclei and protons, $a_{\text{N}(\mu)}$ and $a_{\text{H}(\mu)}$, the hyperfine data include those coupling constants of the ^{13}C - and ^{33}S -isotopes, $a_{\text{C}(\mu)}$ and $a_{\text{S}(\mu)}$, which were determined from the satellite lines in the ESR. spectra. The assignment of all values $a_{\text{N}(1,3)}$ and $a_{\text{S}(2)}$, as well as of $a_{\text{H}(6,7)}$ for $2^\ominus$ and $2^\oplus$, is unequivocal. That of $a_{\text{C}(\mu)}$ and of the remaining proton coupling constants, is based on comparison with analogous experimental data and on their relationships to the π -spin populations ρ_μ at the centres μ [10]. The values ρ_μ were calculated with the aid of HMO models (see discussion) refined by the *McLachlan* treatment [11].

Discussion. - The π -spin distributions in the radical ions of naphtho[1,8-cd]-[1,2,6]thiadiazine (**1**) are most conveniently discussed in terms of a HMO model in which the presence of the three hetero-centres is accounted for by the use of conventional parameters [12]. (Since this model leads to a satisfactory interpretation of the experimental data, we refrained from explicitly invoking 3d-orbitals on the sulfur centre.) The choice of the heteroatom parameters is not crucial, because the shapes of the frontier orbitals do not drastically change when a_{N} and a_{S} are varied from $a+0.5\beta$ to $a+\beta$, and β_{NS} from 0.7β to β ($\beta_{\text{CN}}=\beta$ throughout). Figure 5 depicts the two frontier orbitals for which the LCAO coefficients were calculated using the mean values of these ranges: $a_{\text{N}}=a_{\text{S}}=a+0.75\beta$ and $\beta_{\text{NS}}=0.85\beta$.

The highest occupied orbital (HOMO) of **1**, which exhibits a vertical nodal plane (m) through the sulfur centre (Fig. 5), correlates with the non-degenerate, non-bonding orbital (NBMO) of the phenalenyl π -system. Accordingly, there is a strong resemblance in the shapes of these two orbitals. It is reflected by the π -spin distributions in the radical cation **1** $^\oplus$ and the phenalenyl radical (**4** $^\cdot$), as is evident from comparison of the coupling constants of the protons and the ^{13}C -nuclei in the positions 4, 6, 7 and 9 of the two iso- π -electronic species (**1** $^\oplus$: $a_{\text{H}(4,9)}=0.508$; $a_{\text{H}(6,7)}=0.674$; $a_{\text{C}(4,9)}=0.75$ and $a_{\text{C}(6,7)}=0.93$ mT; **4** $^\cdot$: $a_{\text{H}(1,3,4,6,7,9)}=0.629$ and $a_{\text{C}(1,3,4,6,7,9)}=0.966$ mT [3]).

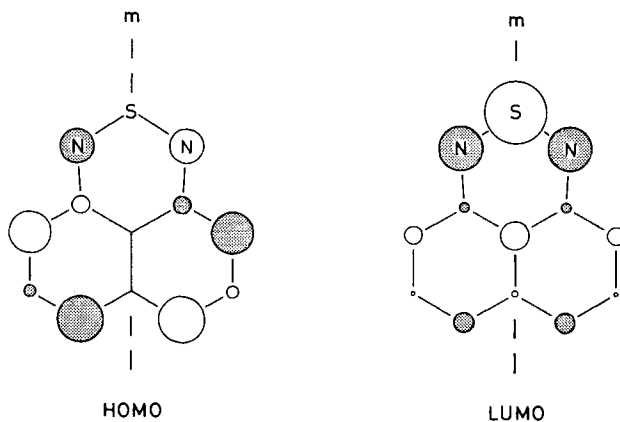


Fig. 5. Highest occupied and lowest unoccupied orbitals (HOMO and LUMO) of naphtho[1,8-cd]-[1,2,6]-thiadiazine (**1**). The areas of the circles are proportional to the squares of the LCAO coefficients. Blank and dotted areas symbolize opposite signs of these coefficients.

On the other hand, the lowest unoccupied orbital (LUMO) of **1**, which is symmetric with respect to the plane *m* (Fig. 5), correlates with one of the doubly degenerate lowest antibonding orbitals of the phenalenyl π -system²⁾. Because of the degeneracy, the introduction of the three hetero-centres affects profoundly the shape of the phenalenyl orbital; the most conspicuous effect is the enormous shift of the orbital population to the thiadiazine fragment. Such a shift is borne out by the observed π -spin distribution in the radical anion **1**^{•−}. The large coupling constants of the ¹⁴N- and ³³S-nuclei ($a_{N(1,3)} = 0.461$ and $a_{S(2)} = 0.89$ mT), which contrast with the small ones of protons ($|a_{H(\mu)}| < 0.15$ mT), clearly indicate that the three hetero-centres accommodate the bulk of π -spin population. This conclusion can also be drawn from the relatively high *g* factor (2.0053) and the considerable *g* and hyperfine anisotropies.

The HMO model of **1** is likewise applicable to 6,7-dihydroacenaphtho[5,6-*cd*]-[1,2,6]thiadiazine (**2**) which represents an alkyl substituted derivative of **1**. In fact, comparison of the hyperfine data for **1**^{•−} and **2**^{•−} (Table) points to almost identical π -spin distributions in the two radical anions. With respect to the pairs of equivalent protons in 4,9- and 6,7-positions of **1**^{•−}, this comparison favours strongly the present assignment of the coupling constants which is reversed relative to that proposed previously [6]³⁾. An increase in $|a_{H(6,7)}|$ by nearly 50 percent, on passing from the protons at the two π -centres of **1**^{•−} to those in the bridging dimethylene chain of **2**^{•−}, is consistent with a dihedral angle of *ca.* 30° between the C(methylene)-H-bond and the 2*p_z*-axis at the adjacent π -centre [13].

Although an analogous comparison of the ¹⁴N- and ¹H-hyperfine data for the radical cations **1**^{•+} and **2**^{•+} (Table) discloses larger differences, the general pattern of the π -spin distribution does not change by introducing a dimethylene chain in the 6,7-positions. Again, such a comparison provides support for the assignment of the coupling constants to protons in **1**^{•+}. The almost two-fold increase in $|a_{H(6,7)}|$, on going from the protons at the π -centres in **1**^{•+} to the methylene protons in **2**^{•+}, is characteristic of positively charged π -radicals. Coupling constants of similar magnitude as that observed for the methylene protons in **2**^{•+} (1.264 mT) are generally found for radical cations in which a dimethylene chain bridges two carbon centres of substantial π -spin populations ($\rho_\mu = 0.20$ to 0.25)⁴⁾.

The π -system of acenaphtho[5,6-*cd*]-[1,2,6]thiadiazine (**3**) differs from that of **1** by two additional carbon centres. Nevertheless, HMO models of **3**, which employ the same heteroatom parameters as those of **1**, predict that the delocalization of the orbital population onto these centres is only moderate for the HOMO and LUMO of **3**. Moreover, these MO's should resemble the corresponding frontier orbitals of **1**. These predictions were verified only in the case of the LUMO, since the short-lived radical cation **3**^{•+} could not be characterized by ESR. spectro-

²⁾ In the HMO model these orbitals are triply degenerate, which is, of course, an artefact of the simple theory.

³⁾ The HMO-McLachlan calculations on **1**^{•−} yield π -spin populations $\rho_{4,9} \approx \rho_{6,7}$. Thus, on this basis alone, the assignment of the coupling constants to protons at the pertinent centres is subject to uncertainty.

⁴⁾ Examples are the coupling constants of the methylene protons in the radical cations of acenaphthene (1.318 mT) [14], pyracene (1.280 mT) [8], and acepleiadene (1.006 mT) [15].

copy (see results). The hyperfine data for the radical anion $3^{\ominus}$ (Table) confirm that the π -spin distributions in $1^{\ominus}$ and $3^{\ominus}$ are indeed similar. In particular, the thiadiazine fragment of $3^{\ominus}$ still houses the bulk of π -spin population. Some displacement from the sulfur to the nitrogen centres is suggested by an increase in $a_{N(1,3)}$ and a decrease in $a_{S(2)}$ observed for $3^{\ominus}$ relative to $1^{\ominus}$.

Source of compounds. Naphtho[1,8-*cd*]-[1,2,6]thiadiazine (**1**) was prepared according to Beecken [16]. The synthesis of 6,7-dihydroacenaphtho[5,6-*cd*]-[1,2,6]thiadiazine (**2**) followed an analogous procedure. For the preparation of acenaphtho[5,6-*cd*]-[1,2,6]thiadiazine (**3**) use was made of a method described by Flowerday *et al.* [17].

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