Chem. Ber. **114**, 2622 – 2631 (1981)

Radical Ions, 46[1–3]

One-Electron Oxidation of 1,8-Chalcogen-Bridged Naphthalenes

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Received December 23, 1980

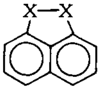
The peri-bridged naphthalenes $C_{10}H_6XY$ with XY = SS, SSe, STe, SeSe, SeTe, TeTe all exhibit low first vertical ionization potentials at about 7.1 eV and, therefore, can be oxidized using $AlCl_3/H_2CCl_2$. The radical cations generated (XY = SS to SeTe) are stable at room temperature. The chalcogen bridges dominate the species $M^{\cdot\oplus}$ regarding spin population as well as charge distribution and, correspondingly, the ESR spectra reflect the effect of increasing spin/orbit interaction S < Se < Te: line widths grow and *g* values raise linearly from 2.0086 (XY = SS) to 2.0409 (XY = SeTe). The PES ionization energies and the ESR coupling constants of sulfur-bridged derivatives are satisfactorily reproduced by a molecular state parametrized HMO model.

Radikalionen, 46[1–3]

Die Einelektronen-Oxidation 1,8-Chalkogen-überbrückter Naphthaline

Die peri-überbrückten Naphthaline $C_{10}H_6XY$ mit XY = SS, SSe, STe, SeSe, SeTe, TeTe weisen alle niedrige erste vertikale Ionisierungspotentiale von etwa 7.1 eV auf und lassen sich daher mit $AlCl_3/H_2CCl_2$ oxidieren. Die erzeugten Radikalkationen (XY = SS bis SeTe) sind bei Raumtemperatur stabil. Die Chalcogen-Brücken prägen die Species $M^{\cdot\oplus}$ sowohl bezüglich der Spinpopulation wie der Ladungsverteilung und dementsprechend spiegeln die ESR-Spektren den Effekt zunehmender Spin/Bahn-Wechselwirkung S < Se < Te wider: Die Linienbreiten wachsen und die *g*-Faktoren erhöhen sich linear von 2.0086 (XY = SS) bis auf 2.0409 (XY = SeTe). Die PES-Ionisierungsenergien und die ESR-Kopplungskonstanten der Schwefel-Derivate werden von einem HMO-Modell mit Molekülzustands-Parametern zufriedenstellend wiedergegeben.

Peri-substituted naphthalenes containing dichalcogen bridges have received renewed interest as potential electron donors in one-dimensional organic charge-transfer conductors[5–7]. A novel and elegant synthesis[6] reacting a THF solution of 1,8-dilithionaphthalene at – 78 °C with powdered chalcogens has been extended successfully to prepare the mixed derivatives with SSe-, STe-, and SeTe-bridges[7]. Starting from known molecular properties of bis(methylthio)-substituted naphthalenes[3] as well as of



$$XX \left\{ \begin{array}{l} SS^{4-6)},\ SeSe^{6)},\ TeTe^{6)} \\ SSe^{7)},\ STe^{7)},\ SeTe^{7)} \end{array} \right. \qquad (1)$$

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naphtho[1,8-*cd*]-1,2-dithiole[4,5], we wish to report the photoelectron spectra of the neutral molecules M and the ESR spectra of their radical cations $M^{\cdot\oplus}$ and to discuss differences along the sequence (1).

A. One-Electron Ionization

The representative photoelectron spectra of naphtho[1,8-*cd*]-1,2-dithiole, -diselenole, and -tellurathiole are presented along with those of naphtho[1,8-*bc*]thiete[7] and of naphtho[1,8-*de*]-1,3-dithiin[8] for assignment in Figure 1; the ionization energies or band maxima, respectively, are compiled in Table 1.

The PE spectra of the naphtho-chalcogen derivatives $C_{10}H_6XY$, each of which contains 58 valence electrons, as expected display numerous overlapping bands especially in the σ ionization region above 11 eV (Figure 1). Therefore, the discussion will be confined to the π ionizations separated at lower energies.

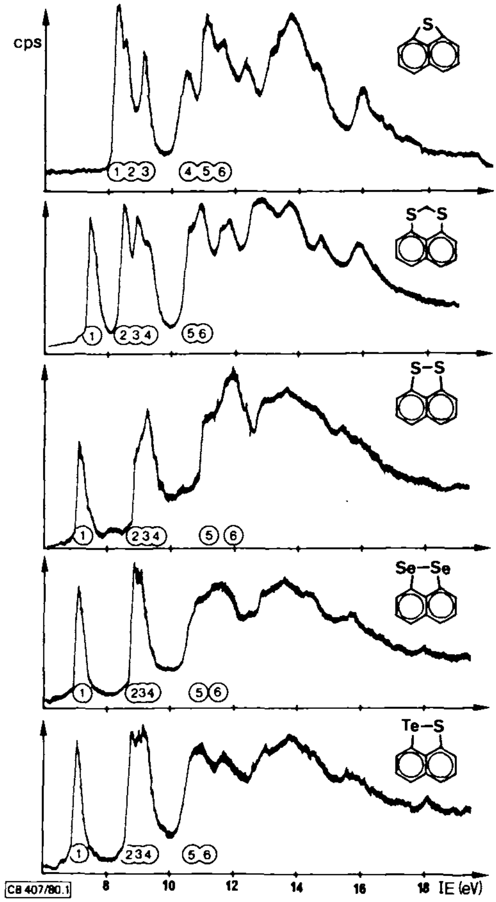
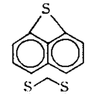
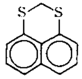
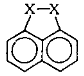
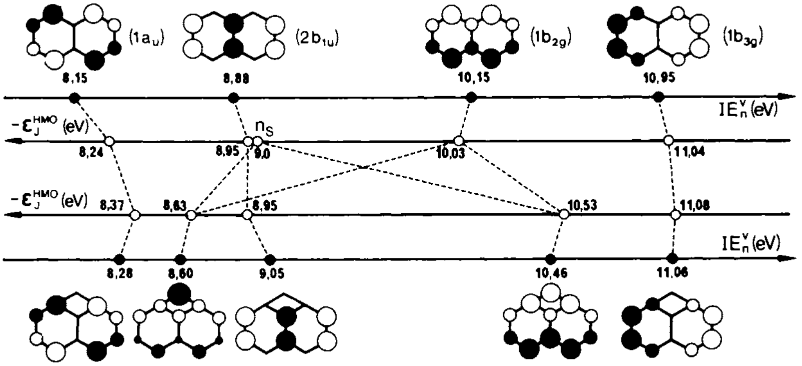


Figure 1. He(I) photoelectron spectra of naphtho[1,8-*bc*]thiete, naphtho[1,8-*de*]-1,3-dithiin, naphtho[1,8-*cd*]-1,2-dithiole, -diselenole and -tellurathiole (encircled numbers refer to Table 1).

Table 1. Vertical ionization energies IE_n^v or band maxima ⓝ in the PE spectra of peri-chalcogen-bridged naphthalene derivatives (cf. Figure 1)

M	XX	①	②	③	④	⑤	⑥	Additional Maxima
		8.28	(8.6)	9.08	10.46	11.02	(11.6)	12.3/(13.1)/(13.7)/ (14.5)/(15.9)
		7.41	8.50	8.81	(9.3)	(10.5)	10.9	(11.9)/(12.8)/(13.7)/ (14.7)/(15.9)
	SS	7.14	(8.9)	(9.1)	(9.4)	(11.1)	(12.0)	(13.1)/(13.8)/(15.4)
	SeS	7.14	8.91	(9.1)	(9.3)	(11.0)	(11.7)	(13.0)/(14.7)/(15.8)
	TeS	7.03	8.70	8.91	9.32	(10.6)	(10.9)	(11.6)/(13.8)/(15.8)
	SeSe	7.06	8.90	9.10	9.21	(10.9)	(11.6)	(13.1)/(13.8)/(15.9)
	TeSe	7.05	(8.7)	(8.9)	(9.0)	(10.6)	(10.9)	(13.0)/(14.0)/(15.8)
	TeTe	7.10	8.80	(9.0)	(9.1)	(10.6)	(11.0)	(11.8)/(13.0)/(15.6)

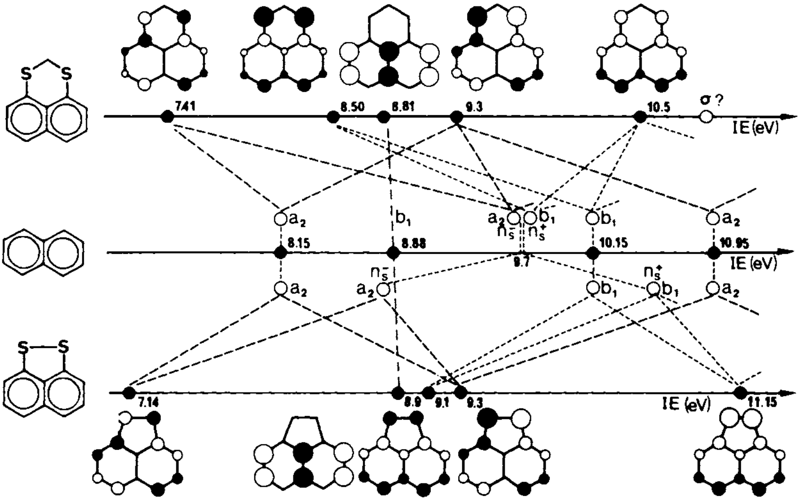
Preferentially, the PES assignment starts from the naphthalene π ionization energies[9].



(2)

As demonstrated in (2) by the *Koopmans'* approximation, $IE_n^v \approx -\varepsilon_J^{HMO}$, they correlate satisfactorily to π eigenvalues of a molecular state-parametrized HMO model[10-13] (cf. (4) and Exp. Part). Introducing the special parameters $\alpha_S = -9.0$ eV and $\beta_{CS} = -1.0$ eV for the naphthothiete-sulfur yields the close prediction (2) of the first five π ionizations of naphtho[1,8-*bc*]thiete (Table 1), which should be planar by analogy to its 1,1-dioxide[8]. Rationalizing orbital-wise: on $D_{2h} \rightarrow C_{2v}$ symmetry reduction, the mixing of the sulfur lone pair n_S with the 2 naphthalene π orbitals, which contain no node through centers 9,10 and display non-zero coefficients at centers 1,8, produces an additional π orbital between π_1 and π_2, and also pushes π_3 to higher energies (2). The first π level of naphthalene remains unperturbed except for a small inductive raise due to sulfur substitution, and this explains the relatively high first ionization potential with respect to the other peri-bridged derivatives investigated (Table 1).

Similar arguments[3] can be applied to the assignment of both the naphtho[1,8-*de*]-1,3-dithiin and naphtho[1,8-*cd*]-1,2-dithiole π ionizations: the PE spectra (Figure 1) each show considerably lowered first energies IE_1 (Table 1). These observations are incorporated into the MO scheme (3) by introducing 2 sulfur lone pairs, either energetically degenerate for the 1,3-dithiin or split by about 1 eV[2,5] in the π MO model for the 1,2-dithiole.



(3)

Formally, in both perturbation schemes (3) the 2 sulfur lone pairs n_S are linearly combined to the orbital pairs n_S^- (a_2) and n_S^+ (b_1). These should interact most strongly with the nearest naphthalene π orbitals of the same irreducible representation a_2 or b_1, respectively, and – as an additional condition – with non-zero coefficients at the substitution centers 1 and 8. Transferring the orbital scheme to radical cation comparison (3), the shifts of the π ionizations relative to naphthalene are rationalized as follows: the ground state $\tilde{X}$ ($^2A_2$) is considerably stabilized by sulfur (n_S^-) contribution. The next 2 $M^{\cdot\oplus}$ states both are of same symmetry, $\tilde{A}$ ($^2B_1$) and $\tilde{B}$ ($^2B_1$), but of different character: for naphtho-1,3-dithiin, the first one contains a dominating sulfur (n_S^+) contribution due to strong mixing with the naphthalene π state at 10.15 eV, whereas in naphtho-1,2-dithiole the unperturbed naphthalene π state $\tilde{A}$ ($^2B_1$) at 8.9 eV comes next. From the perturbation scheme (3), which is nicely confirmed by the near constancy of the π ionizations connected by a dot-dash line, one would trace the $M^{\cdot\oplus}$ ($^2B_1$) state crossing to the degeneracy or nondegeneracy, respectively, of the n_S^-/n_S^+ combinations. The following π states, $\tilde{C}$ ($^2A_2$) and $\tilde{D}$ ($^2B_1$), are tentatively assigned to one sulfur-dominated and one naphthalene-dominated π state of naphtho-1,3-dithiin and to two sulfur-dominated states in naphtho-1,2-dithiole. This assignment of the low energy part of the photoelectron spectra (Figure 1) is nicely confirmed by calculated ionization energies from the parametrized HMO version (cf. Exp. Part or ref.[5]) as well as by *Koopmans'* correlation with CNDO eigenvalues[2,3,5].

For the photoelectron spectra of naphthalene derivatives with Se or Te containing peri-bridges (Figure 1 and Table 1), no essential change in the radical cation state sequence discussed above is to be expected according to HMO parametrized calculations (cf. Exp. Part for e.g. SeSe and TeS derivatives). In return, the optimized parameters

X	C	S	Se	Te
$-\alpha_X$ (eV)	6.0	9.7	9.1	8.5

$-\beta_{XY}$ (eV)	C	S	Se	Te
C	3.1	2.0	1.5	1.2
S		1.3[14)]	1.1	0.9
Se			0.9	0.7
Te				0.6

(4)

in eV (4) give some clues how inductive perturbations, $-\alpha_X$ and conjugative interactions $-\beta_{XY}$, respectively, change along the series: thus the inductive shift to lower π ionization energies in tellurium-containing derivatives is counteracted by the reduced second order perturbation[13)]. Therefore, the first ionization energies of all derivatives are expected and observed within a narrow range (Table 1: 7.03 eV to 7.14 eV). The same holds for the PES region around 9 eV: 3 bands are predicted and – partly overlapping – are found (Figure 1).

Summarizing, the PE spectra of the relatively large naphthalene molecules with 1,8-chalcogen bridges display distinguishable bands only in their low-energy region. These can be assigned transparently by radical cation state comparison (cf. (2) and (3)) based on a topological MO model which has been parametrized using PES ionization energies. Most intriguing, however, are the rather low first ionization potentials of the naphtho[1,8-*cd*]-1,2-dichalcogenoles, which suggest that all compounds $C_{10}H_6XY$ might well be oxidized by the oxygen-free $AlCl_3/H_2CCl_2$ system[2,3,14)] in solution to their radical cations.

B. One-Electron Oxidation

According to their first ionization potentials below 8 eV[14)], the naphtho[1,8-*cd*]-1,2-dichalcogenoles can be oxidized by $AlCl_3$ in H_2CCl_2 to their radical cations; the only exception being the ditellurium derivative for which no ESR signal could be detected even at 200 K. The ESR spectra (Figures 2 and 3) show line widths increasing in the nuclear sequence S > Se > Te: from the 17 lines observed for the disulfide radical cation, only a quintet remains in the selenothiole derivative, it still is recognizable in the ESR spectrum of $C_{10}H_6SeSe^{\bullet\oplus}$ but can no longer be detected for $C_{10}H_6TeSe^{\bullet\oplus}$. All the ESR data are summarized in Table 2.

The naphtho[1,8-*cd*]-1,2-dithiole radical cation has been generated repeatedly[4,17,18)]. In view of the partly contradicting results reported, a computer simulation of its ESR spectrum is shown in Figure 2, which has been achieved using the coupling constants from Table 2. Increasing the line widths in the simulations leads to a quintet as documented for $C_{10}H_6SSe^{\bullet\oplus}$ (Figure 3). Therefore, all less-resolved ESR spectra (Figure 3: $C_{10}H_6SeSe^{\bullet\oplus}$ and $C_{10}H_6TeSe^{\bullet\oplus}$) are assumed to originate as well from 2 larger and one smaller proton couplings. In agreement also with the almost identical first ionization energies of the individual derivatives (Table 1), the spin distribution ratio between the naphthalene π system and the chalcogen bridges should be of the same order of magnitude in all radical cations generated in solution.

The experimental π spin populations ρ_μ^{exp} as deduced from the *McConnell* approximation, $\rho_\mu^{\text{exp}} \approx a_{\text{H},\mu}|Q|$[19)], are comparable to the ones calculated, $\rho_\mu^{\text{calc.}}$, using the parametrized HMO program in the *McLachlan* approximation[20)] (cf. Exp. Part): obviously, even the numerical correspondence is mostly satisfactory (Table 2). Therefore, a comparison of the otherwise inaccessible spin populations of the chalcogen bridges can be accomplished: they are constant along the series $SS^{\cdot\oplus}$, $SSe^{\cdot\oplus}$, $SeSe^{\cdot\oplus}$ and thus confirm the orbital picture developed to assign the PE spectra (3), which suggests that in the

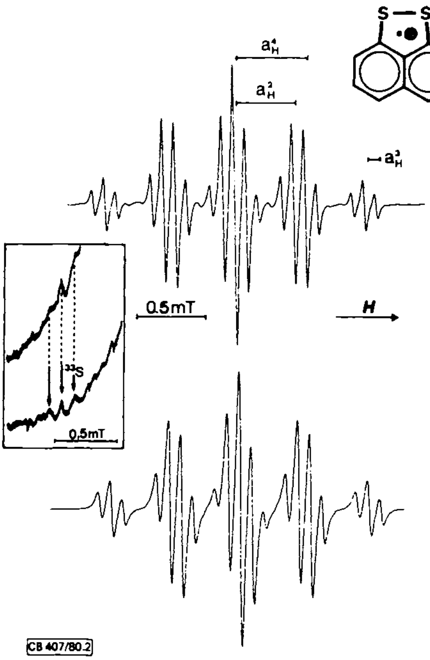


Figure 2. ESR spectrum of the naphtho[1,8-*cd*]-1,2-dithiole radical cation at 200 K and its computer simulation. Insert: ^{33}S coupling in the extremely amplified low-field tale.

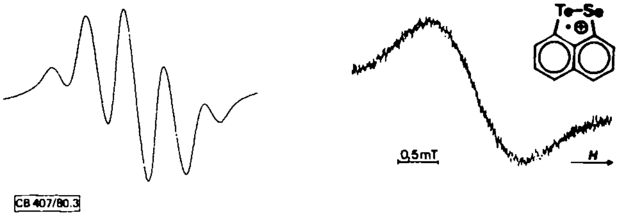
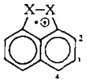
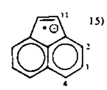
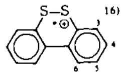


Figure 3. ESR spectra of some naphthalene radical cations containing dichalcogen peri-bridges: $C_{10}H_6SeS^{\cdot\oplus}$ (with computer simulation), $C_{10}H_6SeSe^{\cdot\oplus}$ and $C_{10}H_6TeSe^{\cdot\oplus}$, all generated with $AlCl_3/H_2CCl_2$ at 200 K.

Table 2. ESR data of naphtho[1,8-*cd*]-1,2-dichalcogenole radical cations and of acenaphthylene radical anion as well as 2,2'-biphenyldiyl disulfide radical cation for comparison

Radical Ion	XX	μ	g	$a_{(H)\mu}$(mT)	$\rho_\mu^{exp.}$(mT)[a]	$\rho_\mu^{calc.}$
	SS	2		.432	.168	.151
		3		.092	.036	$-.033$
		4	2.0086	.525	.204	.216
		S		.733		.153
	SeS	2/7		.44	.17	.135
		3/6		.08	.03	$-.029$
		4/5	2.0209	.48[b]	.19	.211
		S				.147
		Se				.164
	TeS		2.0318	[c]		
	SeSe	2		.37	.14	.121
		3		.06[a]	.02	$-.024$
		4	2.0397	.43	.17	.190
		Se				.153
	TeSe		2.0409	[c]		
 [15]		2		.451	.196	.205
		3		.045	.020	$-.052$
		4	2.0027	.565	.245	.261
		11		.309	.134	.100
 [16]		3		.01	.004	.001
		4		.038	.015	$-.006$
		5	2.0112	.098	.038	.045
		6		.183	.071	.053
		S		1.09		.235

[a] Nach *McConnell*[19] $\rho_\mu^\pi = a_{H,\mu}/|Q|$ mit $|Q^\oplus| = 2.57$ mT or $|Q^\ominus| = 2.30$ mT. – [b] Not detectable due to large line-widths. – [c] Single broad line.

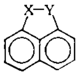
radical cation ground state most of the spin is localized within the naphthalene π system. This interpretation is further substantiated by comparison of the iso(valence)-electronic acenaphthylene radical anion (Table 2): on substitution of 2 CH units by 2 sulfurs, the spin population changes only slightly. Relative to the naphthalene radical cation ($a_{H,1} = 0.554$ mT and $a_{H,2} = 0.206$ mT)[21], the coupling increases in 2-position and decreases in 3-position (Table 2).

As concerns the sulfur spin population, several ^{33}S isotope couplings ($I(^{33}S) = 3/2$, nat. abundance 0.74%) have been reported, e.g. for the 2,2'-biphenyldiyl disulfide radical cation[16] (Table 2). Later on, a *McConnell*-type linear regression, $a_{^{33}S} = |Q_{^{33}S}|\,\rho_S$, has been proposed with $Q_{^{33}S} \approx 3.3$ mT[18]. Although this approach allows reasonable estimates, the simplification is a considerable one with respect to the more general *Karplus/Fraenkel* relation, $a_X = Q_X\rho_X + \sum_Y Q_{YX}\,\rho_Y$[22]. ESR-investigation of 1,4-dithiin radical cations[23] or of thiomaleic anhydride radical anions[24] suggest $Q_{CS} \approx 0$ mT. However, neglect of the adjacent disulfide sulfur center seems unjustified: based on our *McLachlan* calculations (cf. Exp. Part), a rather substantial value $Q_{SS} = +1.3$ mT is deduced. This nicely reproduces not only known $a_{^{33}S}$ coupling constants – e.g. in

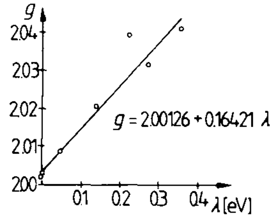
2,2′-biphenyldiyl disulfide (exp. 1.09 mT[16], calc. 1.08 mT) or naphtho[1,8-*cd*: 4,5-*c′d′*]-bis[1,2]dithiole (exp. 0.453 mT[2] or 0.447 mT[18], calc. 0.465 mT) – but predicted correctly the ^{33}S coupling for the naphtho[1,8-*cd*]-1,2-dithiole radical cation (calc. 0.704 mT), which subsequently could be detected (Table 2: 0.733 mT, cf. also 0.716 mT[18]) in the extremely amplified low-field range of the ESR spectrum (Figure 2: insert). Its triplet with ≈ 0.3% intensity (calc. 0.37%) displays the proton coupling $a_{H,3}$ = 0.092 mT (Table 2).

Two other characteristic ESR spectroscopic features of the peri-bridged naphthalene radical cations investigated are the line widths (Figures 2 and 3) and the g-values (Table 2). Both are interrelated with spin orbit coupling which increases with increasing element number within each group of the periodic table (λ_S = 0.05 eV, λ_{Se} = 0.22 eV and λ_{Te} = 0.49 eV)[25]. As for the line widths: with increasing spin orbit coupling the spin lattice relaxation i.e. the longitudinal relaxation time decreases and, therefore, the line-width increases[26]. Looking at the ESR spectra, only the one for the disulfide is resolved, the signals for the diselenide overlap strongly, and the $TeSe^{\cdot\oplus}$ derivative only displays one broad line (Figures 2 and 3).

The g-values of the radical cations generated also differ considerably from each other as well as from the one for the free electron, g = 2.0023[26]. Deviations are discussed in terms of admixture of excited states[26], increasing with spin orbit coupling λ (5).

$e^{\ominus}$		$CC^{\cdot\ominus}$	$SS^{\cdot\oplus}$	$SSe^{\cdot\oplus}$	$STe^{\cdot\oplus}$	$SeSe^{\cdot\oplus}$	$SeTe^{\cdot\oplus}$	
2.0023	g	2.0027	2.0086	2.0209	2.0318	2.0397	2.0409	(5)
0.0	λ (eV)	0.0037	0.05	$\overline{0.14}$	$\overline{0.27}$	0.22	$\overline{0.36}$	

With the spin populations in the chalcogen bridges as being discussed approximately constant, one expects and finds a linear regression with only small standard deviation SE = 0.00253 (g-units) (6).



(6)

Summarizing, the chalcogen substituent perturbations of the naphthalene π systems are of the same order of magnitude because different effective nuclear charges for S, Se, Te and different bond lengths d_{CX} and d_{XX} largely compensate each other. This becomes evident especially in the almost constant first ionization energies (Table 1) of the neutral molecules and in the almost identical peri-bridge chalcogen spin populations of the radical cations (Table 2). Nevertheless, considerable differences are displayed in the ESR spectra due to increasing spin orbit coupling S < Se < Te: line widths broaden to single signal ESR spectra (Figure 3), and g-values grow up to 2.0409 (Table 2).

Acknowledgment. Our research has been supported generously by *Land Hessen, Deutsche Forschungsgemeinschaft,* and *Fonds der Chemischen Industrie.*

Experimental Part

Photoelectron spectra have been recorded on a Perkin-Elmer PS 16 spectrometer equipped with a heated inlet system and were calibrated using the $Xe(^2P_{3/2})$ = 12.13 eV and $Ar(^2P_{3/2})$ = 15.76 eV peaks.

Radical cation generation was performed in 2 mm-i.d. glass capillary tubes under N_2 by the following procedure: 1 mg of the compound was dissolved in 0.1 ml of oxygen-free dichloromethane, which had been kept dry over $AlCl_3$, and ~ 5 mg of $AlCl_3$ was added to this solution.

Electron spin resonance spectra were recorded using a Varian E9 spectrometer, equipped with an E 257-variable temperature unit, at 9.5 GHz-frequency and 330 mT-magnetic field, and a field modulation of 100 kHz. The proton coupling constants a_H (cf. Table 2) are assumed to be correct within ± 1%; calibration was performed with Fremy's salt ($2a_N$ = 2.618 mT). g-Values were determined by the double cavity technique using perylene radical anion in DME for calibration[27].

ESR spectra simulation could be achieved using the program ESPLOT[28].

Compounds have been synthesized according to the literature procedures[6-8] and were analytically pure:

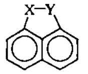
$C_{10}H_6Se_2$ (284.1)	Calc.	C 42.28	H 2.12	Se 55.59	
	Found	C 42.26	H 2.12	Se 55.46	
$C_{10}H_6Te_2$ (381.4)	Calc.	C 31.49	H 1.59	Te 66.92	
	Found	C 31.31	H 1.60	Te 67.12	
$C_{10}H_6SSe$ (237.2)	Calc.	C 50.64	H 2.55	S 13.52	Se 33.30
	Found	C 50.58	H 2.53	S 13.55	Se 33.64
$C_{10}H_6STe$ (285.8)	Calc.	C 42.02	H 2.11		
	Found	C 42.06	H 2.00		
$C_{10}H_6SeTe$	(333.8681), *m/e*: 333.8679				
$C_{10}H_6S$ (158.2)	Calc.	C 75.91	H 3.82	S 20.76	
	Found	C 75.85	H 3.74	S 20.18	

HMO parametrization: PE ionization energies – especially those producing radical cation states of unique symmetry – have been used as described in detail elsewhere[10-13] to obtain parameters α_X and β_{XY} either in eV (4) or h_X and k_{XY} in units β (7).

X	C	S	Se	Te
h_X	0.0	1.2	1.0	0.8

k_{XY}	C	S	Se	Te
C	1.0	0.65	0.5	0.4
S		0.42	0.35	0.30
Se			0.30	0.22
Te				0.20

(7)

	XY		①	②	③	④	⑤
	SS	IE_n (eV)	7.14	8.91	9.07	9.35	11.15
		$-\varepsilon_J^{HMO}$ (eV)	7.09	9.10	9.31	9.40	11.28
	SeSe	IE_n (eV)	7.06	8.95	9.09	9.20	10.95
		$-\varepsilon_J^{HMO}$ (eV)	7.20	9.01	9.10	9.18	10.88
	TeS	IE_n (eV)	7.03	8.78	8.91	9.29	10.6
		$-\varepsilon_J^{HMO}$ (eV)	7.20	8.55	8.90	9.11	10.44

(8)

The HMO program version (adapted to a PDP/40 and available on request) allows predictions of π ionization energies of S-, Se- or Te-substituted aromatic systems as demonstrated in (2) or (8).

Via the *McConnell* relation, $a_{H,\mu} = |Q| \rho_\mu$[19], ESR coupling constants for the ring protons are also reproduced satisfactorily. Alternatively, a *McLachlan* improvement including polarizabilities[20] can also be achieved using $\lambda = 1.2$ (cf. Table 2).

CNDO closed shell and INDO open shell calculations have been performed using the QCPE version at the Hochschul-Rechenzentrum of the University Frankfurt.

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