

Heterocyclic Radicals. Part III.^{1,2} An Electron Spin Resonance Investigation of Some Selenium-containing Radicals

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The isotropic e.s.r. spectra of a number of selenium-containing aromatic radicals are reported. The variations of the line-widths of these spectra are described and discussed semi-quantitatively in terms of spin-orbit and spin-rotational relaxation mechanisms. Simple Hückel and McLachlan MO calculations are employed to account for the observed hyperfine splittings, including those from ⁷⁷Se, and to assist with their assignment where necessary. Finally, a semi-empirical theory of *g*-values for aromatic radicals is used to account for the observed *g*-shifts.

In the course of our investigation² into the e.s.r. spectra of radicals from phenothiazine and related compounds, we detected ⁷⁷Se hyperfine splittings and anomalous line-width behaviour for the radical cation and the nitroxide from phenoselenazine. We now report a more detailed study of these selenium-containing radicals and an exten-

¹ Part I, B. C. Gilbert, R. O. C. Norman, P. Hanson, and B. T. Sutcliffe, *Chem. Comm.*, 1966, 161.

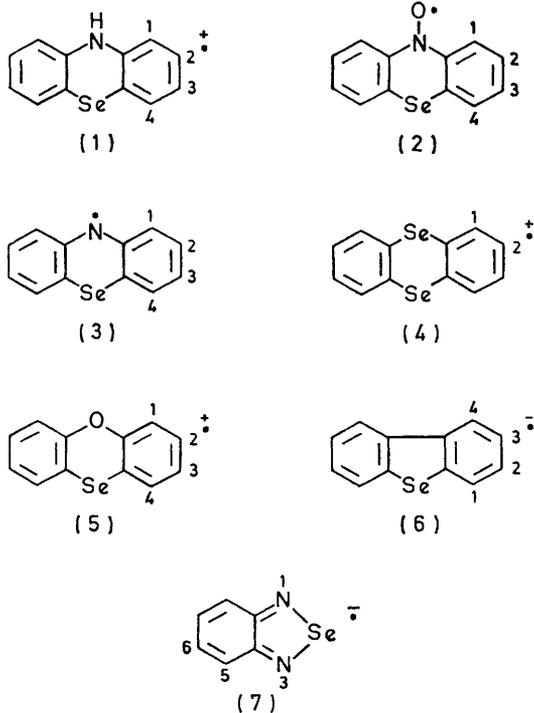
sion of this investigation to other selenium-substituted cyclic radicals of different type.

The scarcity of data on organoselenium radicals may reflect, at least in part, the difficulty in achieving high resolution. Thus, although proton splittings and ⁷⁷Se splittings (⁷⁷Se has $I = \frac{1}{2}$, natural abundance 7.5%) have

² Part II, M. F. Chiu, B. C. Gilbert, and P. Hanson, *J. Chem. Soc. (B)*, 1971, 1700.

been resolved for the selenium radicals mentioned above² and for some highly hindered phenoxy-radicals with *para*-selenium-containing substituents,³ the radical cations from phenoxselenin and dibenzoselenin, generated⁴ in 95% sulphuric acid, have line-widths so great that resolution of hyperfine splittings is impossible.

In contrast, relatively narrow e.s.r. spectra have been reported for the radical anions of dibenzoselenophen (prepared⁵ from the parent compound by alkali-metal reduction in dimethoxyethane) and 2,1,3-benzoselenadiazole (prepared by reduction with potassium *t*-butoxide in dimethyl sulphoxide-*t*-butyl alcohol,⁶ by electrolytic reduction,⁷ and by reaction with alkali metals in a variety of solvents⁸). The radical anion of tetrafluoro-2,1,3-benzoselenadiazole has been prepared⁹ from the parent compound with sodium in tetrahydrofuran and it exhibits a fairly broad-lined e.s.r. spectrum, and the e.s.r. spectrum of phenylselenoxanthyl has also been reported.¹⁰ In none of these studies was ⁷⁷Se hyperfine interaction reported. It is interesting that the appreciable line-width for the 2,1,3-benzoselenadiazole radical anion has been observed⁷ to decrease with decreasing temperature, giving improved resolution (*cf.* the phenoselenazine nitroxide and radical cation²).



Most of the above-mentioned reports were primarily concerned with the corresponding sulphur-containing

³ E. Müller, H. B. Stegmann, and K. Scheffler, *Annalen*, 1962, **657**, 5.

⁴ B. Lamotte and G. Berthier, *J. Chim. phys.*, 1966, **63**, 369.

⁵ R. Gerdil and E. A. C. Lucken, *J. Amer. Chem. Soc.*, 1965, **87**, 213.

⁶ E. T. Strom and G. A. Russell, *J. Amer. Chem. Soc.*, 1965, **87**, 3326.

⁷ N. M. Atherton, J. N. Ockwell, and R. Dietz, *J. Chem. Soc. (A)*, 1967, 771.

radicals (*e.g.*, in providing an assessment of the importance of *d*-orbital participation) and relatively little emphasis has been placed on the properties of the selenium analogues other than for comparison. Accordingly, we have attempted to prepare a variety of organoselenium radicals in solution in order to examine the dependence of their spectra upon temperature and, in particular, to investigate the variations in line-width and $a(^{77}\text{Se})$ with radical structure. In addition to our experimental findings, we here report MO calculations, using the Hückel and McLachlan¹¹ methods, and our suggestions for suitable parameters for selenium in a variety of radicals. The radicals chosen include the phenoselenazine radical cation (1), phenoselenazine nitroxide (2), phenoselenazine neutral radical (3), the dibenzodiselenin radical cation (4), the phenoxselenin radical cation (5), the dibenzoselenophen radical anion (6), and the 2,1,3-benzoselenadiazole radical anion (7).

EXPERIMENTAL

All spectra were obtained on a Varian E-3 e.s.r. spectrometer in conjunction with a V-4540 Variable Temperature Accessory; our previous² experimental investigations of compounds (1) and (2) were not repeated. Coupling constants and *g*-values were determined by comparison with those of *p*-benzosemiquinone¹² and were verified by computer simulation by use of a FORTRAN IV programme in which Lorentzian line-shape was assumed. An option was included to allow the simulation of satellite lines from low-abundance isotopes. Except where stated otherwise, the maximum error in the coupling constants is estimated to be less than 1%.

Solvents were of reagent grade and in all cases, except where mentioned otherwise, chemicals were commercial samples which were recrystallised before use. A sample of dibenzoselenophen, kindly supplied by Mr. A. J. G. Crawshaw, was recrystallised from carbon tetrachloride.⁵ The neutral phenoselenazine radical was prepared by the oxidation of a deoxygenated solution of phenoselenazine in dry benzene (*ca.* 10⁻⁴M) with lead dioxide (see ref. 2); solutions were stable at room temperature for *ca.* 30 min. The earlier work⁴ on the dibenzodiselenin radical cation was not repeated; the radical cation of phenoxselenin was prepared under nitrogen by oxidation of the parent heterocycle with aluminium trichloride in dry deoxygenated nitroethane¹³ and the radical anions of dibenzoselenophen and 2,1,3-benzoselenadiazole were prepared by conventional vacuum-line techniques by reduction with a potassium mirror in dimethoxyethane (dried by distillation twice from a potassium mirror *in vacuo*). For the dibenzoselenophen radical anion, low temperatures (*ca.* -50 °C) were necessary for preparation and handling in order to obtain stable solutions suitable for e.s.r. study. The other radical anion was

⁸ M. Kamiya and Y. Akahori, *Bull. Chem. Soc. Japan*, 1970, **43**, 268.

⁹ J. Fajer, B. H. J. Bielski, and R. H. Felton, *J. Phys. Chem.*, 1968, **72**, 1281.

¹⁰ K. Maruyama, M. Yoshida, and K. Murakami, *Bull. Chem. Soc. Japan*, 1970, **43**, 152.

¹¹ A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.

¹² B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **43**, 4191.

¹³ W. F. Forbes and P. D. Sullivan, *J. Amer. Chem. Soc.*, 1966, **88**, 2862.

more stable, and solutions could be prepared and handled at room temperature.

Viscosity measurements on dimethoxyethane were carried out by use of a comparative viscometer. Benzene was used as a reference, and viscosities were determined at 10, 20, 30, and 41 °C. Owing to the difficulty of performing viscometry at temperatures below 0 °C, the viscosity of dimethoxyethane between -80 and 0 °C was calculated by extrapolation

RESULTS AND DISCUSSION

The analyses of the e.s.r. spectra of the radicals are given in Table 1.

E.s.r. Spectra.—The variations in line-width with temperature. We have previously drawn attention to the unusual line-width behaviour for the spectrum of the cation radical (1) in nitroethane: the increased resolution

TABLE 1
Calculated and experimental splittings for some selenium-containing radicals ^a

Radical	Position <i>i</i>	Atom <i>x</i>	Calculated splittings (and spin densities)		Experimental <i>a_i²/mT</i>	<i>g</i>
			<i>a_i²/mT</i> HMO	<i>a_i²/mT</i> McLachlan		
(1)	1	H	-0.1278(0.047)	-0.1437(0.055)	(-)0.118 ^b	2.0161 ^b
	2	H	-0.0860(0.032)	-0.0307(0.011)	(-)0.040	
	3	H	-0.2100(0.078)	-0.2398(0.089)	(-)0.250	
	4	H	-0.0185(0.007)	+0.0711(-0.026)	(+)0.040	
		Se	+2.03(0.163)	+2.43(0.198)	(+)2.50	
		N	+0.533(0.192)	+0.653(0.235)	(+)0.617	
(2)	1	H	-0.1539(0.057)	-0.2274(0.084)	(-)0.215 ^b	2.0071 ^b
	2	H	-0.0378(0.014)	+0.0616(-0.023)	(+)0.064	
	3	H	-0.1858(0.069)	-0.2424(0.083)	(-)0.212	
	4	H	-0.0118(0.004)	+0.0804(-0.030)	(+)0.064	
		Se	+1.20(0.096)	+0.822(0.067)	(+)0.770	
		N	+0.694(0.232)	+0.931(0.310)	(+)0.926	
(3)	1	H	-0.1952(0.072)	-0.3048(0.113)	(-)0.382	2.0104
	2	H	-0.0409(0.015)	+0.0772(-0.029)	(+)0.100	
	3	H	-0.2274(0.084)	-0.2927(0.108)	(-)0.286	
	4	H	-0.0143(0.005)	+0.0981(-0.036)	(+)0.100	
		Se	+1.38(0.111)	+1.04(0.085)	(+)1.09	
		N	+0.485(0.294)	+0.714(0.433)	(+)0.696	
(4)	1	H	-0.0358(0.013)	+0.086(-0.003)		2.0315 ^c
	2	H	-0.1405(0.052)	-0.1132(0.042)		
		Se	+2.61(0.207)	+3.43(0.273)		
(5)	1	H	-0.0340(0.013)	+0.0585(-0.022)		2.0228
	2	H	-0.1642(0.061)	-0.2025(0.075)		
	3	H	-0.1517(0.056)	-0.0852(0.032)		
	4	H	-0.0434(0.016)	-0.0185(0.007)		
		Se	+2.95(0.238)	+4.43(0.360)	(+)3.95	
(6)	1	H	-0.1462(0.054)	-0.0701(0.026)	(-)0.103	2.0030
	2	H	-0.4242(0.157)	-0.5656(0.209)	(-)0.518	
	3	H	-0.0113(0.004)	+0.1340(-0.050)	(+)0.103	
	4	H	-0.3268(0.121)	-0.4243(0.157)	(-)0.421	
		Se	+0.206(0.016)	+0.16(0.009)	(+)0.544	
(7)	1	N	+0.622(0.242)	+0.775(0.301)	(+)0.579	2.0063
	2	Se	+2.21(0.179)	+2.63(0.214)	(+)0.49	
	5	H	-0.186(0.069)	-0.199(0.074)	(-)0.248	
	6	H	-0.151(0.056)	-0.081(0.030)	(-)0.165	

^a See text for *Q* values, molecular orbital parameters, solvents, temperatures, and line-widths. ^b Experimental values from ref. 2. ^c Ref. 4.

from the high-temperature values by use of equation (1) ¹⁴ with $\Delta E_{\text{vis}} = 7.903 \text{ kJ mol}^{-1}$ and $\ln \eta_0 = -10.97$ (η_0 in $\text{kg m}^{-1} \text{ s}^{-1}$).

$$\eta = \eta_0 \exp[\Delta E_{\text{vis}}/RT] \quad (1)$$

FORTTRAN IV computer programmes for performing HMO and McLachlan ¹¹ calculations were kindly made available by Dr. D. R. Burnham and were executed on an ICL 4130 computer.

¹⁴ 'Technique of Organic Chemistry,' vol. VII (Organic Solvents), eds. A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, jun., 2nd edn., Interscience, New York, 1955, p. 23.

¹⁵ R. Wilson and D. Kivelson, *J. Chem. Phys.*, 1966, **44**, 154.

on going from room temperature to *ca.* -28 °C, where a minimum in the line-width (*ca.* 0.040 mT) was detected, was attributed to a spin-rotation interaction ¹⁵ which apparently depends on T/η , where T is the temperature (in K) and η is the viscosity. This interaction is expected ¹⁶⁻¹⁹ to be appreciable for radicals with a large isotropic *g*-shift from the value for the free electron (rather than a large anisotropy in *g*), and it is hence

¹⁶ G. K. Fraenkel, *J. Phys. Chem.*, 1967, **71**, 139.

¹⁷ P. W. Atkins and D. Kivelson, *J. Chem. Phys.*, 1966, **44**, 169.

¹⁸ J. R. Thomas, *J. Amer. Chem. Soc.*, 1966, **88**, 2064.

¹⁹ G. Nyberg, *Mol. Phys.*, 1967, **12**, 69.

understandable that, under comparable conditions, the line-width for (1), for which $g = 2.0161$, is much greater than that for the nitroxide (2), for which $g = 2.0071$.² Indeed, we have been unable to resolve completely or to obtain detailed measurements of ΔH for the spectra from (1).

We are now able to compare the line-widths for the related nitroxide (2) and the neutral radical (3), for which $g = 2.0104$. Well-resolved spectra from both radicals were recorded for their solutions in benzene; Figure 1 shows the spectrum of the neutral radical with (inset) the ⁷⁷Se satellites. For both radicals, raising the temperature from 20 to 60 °C leads to an increase in line-width which is reversible, suggesting that spin-rotation is dominant in this range. The spectra also sharpened on going from 20 °C down to the freezing point of the solvent. At a given temperature, the line-width for the neutral radical is somewhat larger than that for the nitroxide: *e.g.*, at 20 °C, for lines with $\tilde{m}_N = -1$, $\Delta H(3) = 0.040 \pm 0.003$ mT and $\Delta H(2) = 0.020 \pm 0.003$ mT. Quantitative measurements of the temperature coefficient of ΔH for the neutral radical (*cf.* $-2.5 \mu\text{T}$ per 10 °C for the nitroxide²) were not possible because of irreversible radical decay at higher temperatures.

Similarly, the instability of solutions of the radical anion of dibenzoselenophen (6) in dimethoxyethane at temperatures above -30 °C precluded detailed measurement of the variation of ΔH with temperature. Figure 2 shows the e.s.r. spectrum at -60 °C with (inset) the low-field satellite from selenium-77 splittings; this spectrum was satisfactorily simulated with a line-width of 0.020 mT (0.022 mT for the satellites). The lines appeared to broaden slightly as the temperature was raised within the limited range available (-60 to -40 °C). The g -value

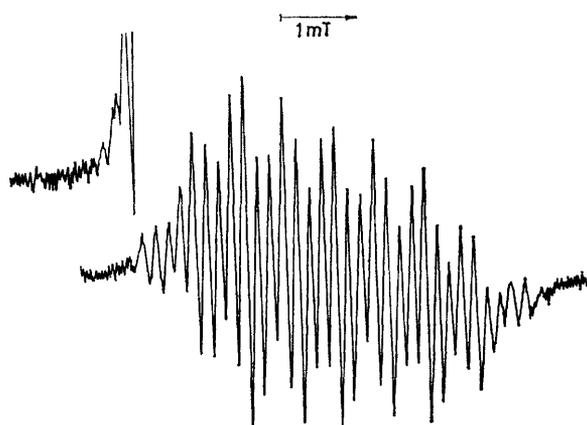


FIGURE 1 E.s.r. spectrum of the phenoselenazine neutral radical in benzene at 20 °C with (inset) the ⁷⁷Se satellites

was determined as 2.0030, much the lowest for the selenium radicals we examined, in keeping with the observation that the lines are fairly sharp and largely unaffected by contributions from spin-rotation interaction.

For the phenoxselenin radical cation (5), prepared in solution in nitroethane, a broad featureless line was

obtained (peak-to-peak width, 0.48 mT at 20 °C): the g -value we estimate as 2.0228, and we also observed ⁷⁷Se satellites with a noticeable high-field broadening which

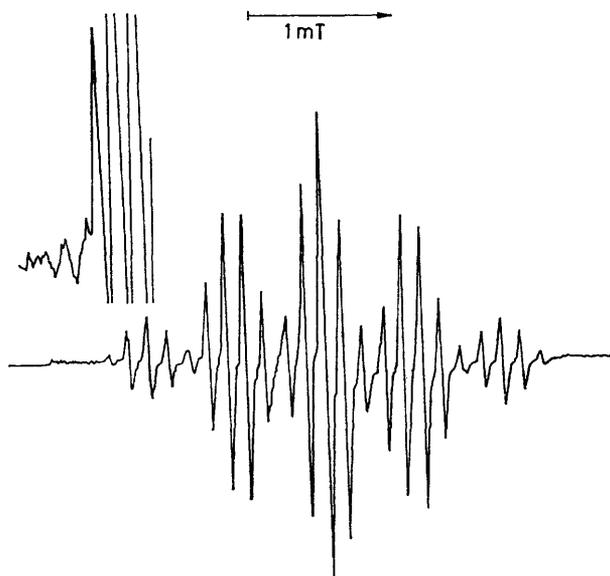


FIGURE 2 E.s.r. spectrum of the radical anion of dibenzoselenophen in dimethoxyethane at -60 °C with (inset) the ⁷⁷Se satellites

indicates that the ⁷⁷Se splitting is positive.² (Lamotte and Berthier⁴ reported a single broad line and $g = 2.0225 \pm 0.005$ for this species, and a broader line, with $\Delta H = 9.3$ G and $g = 2.0315 \pm 0.0010$ for the dibenzodiselenin radical cation.) It proved impossible to resolve the spectrum of (5), even over a wide range of temperature (-60 to $+80$ °C) and microwave power; somewhat surprisingly, the change in overall line-width was scarcely significant, suggesting that if spin-rotation makes a contribution to the line-width (proportional to T/η) then there may also be a significant contribution from the ordinary spin-orbit effect (*i.e.*, from anisotropy in g , and proportional to η/T :¹⁶ see below).

TABLE 2

Variation with temperature of the line-width^a of the central line in the e.s.r. spectrum of the radical anion from 2,1,3-benzoselenadiazole in dimethoxyethane

T/K	$\Delta H/\text{mT}$ (obs.)	$\Delta H/\text{mT}$ (calc.) ^b
192	0.046	0.0474
199	0.046	0.0454
206	0.044	0.0446
216	0.048	0.0454
227	0.050	0.0484
253	0.054	0.0622
256	0.067	0.0644
268	0.075	0.0739
291	0.098	0.0968

^a Peak-to-peak, first derivative. ^b Using the relationship $\Delta H/\text{mT} = 0.0148 + 1.82 \times 10^3 \eta/T + 1.23 \times 10^{-7} T/\eta$ where $\eta/\text{kg m}^{-1} \text{s}^{-1}$ is the viscosity and T/K is the temperature.

Spin-rotational interaction is most markedly illustrated by the line-width dependence on temperature for the radical (7) in dimethoxyethane (see Table 2). At room

temperature the line-width is approximately 0.1 mT and, under these conditions, the proton splittings from positions 5 and 6 appear to be equivalent.⁸ As the temperature is lowered however, the resolution of the low- and mid-field lines ($m_N = -2, -1, \text{ and } 0$) improves and at -80°C the line-width of the central line is less than 0.05 mT. The high-field lines remain broad, probably because of the usual high-field broadening associated with anisotropy in the nitrogen splitting.¹⁶

Inspection of the variation of ΔH (central line) with temperature suggests that a reasonable account can be obtained if contributions proportional to T/η (spin-rotation) and η/T (spin-orbit) are included, as in equation (2). Bilinear regression analysis of the observed

$$\Delta H_{\text{total}} = \Delta H_{\text{natural}} + A_1\eta/T + A_2T/\eta \quad (2)$$

widths yields equations (3) and (4) with $\Delta H_{\text{natural}} = 0.0148$ mT. The line-widths calculated from this

$$A_1 = 1.82 \times 10^3 \text{ kg}^{-1} \text{ m s mT K} \quad (3)$$

$$A_2 = 1.23 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1} \text{ mT K}^{-1} \quad (4)$$

empirical expression are given in Table 2. We calculate that at 80°C the spin-rotation contribution is 0.010 mT and the spin-orbit contribution is 0.022 mT: these become 0.018 and 0.013 mT, respectively, at -60°C , and 0.082 and 0.002 mT, respectively, at 20°C . At this temperature, the spin-rotation term clearly dominates.

It has been shown¹⁷ that for a hydrodynamically spherical molecule of cylindrical magnetic symmetry, for which Δg_{\parallel} is much smaller than Δg_{\perp} (so that $2\Delta g_{\perp} = 3\Delta g_{\text{iso}}$), the relaxation time (in radians s^{-1}) arising from spin-rotation interaction can be approximated as (5),

$$T_2^{-1} = (\Delta g_{\text{iso}})^2/2\tau \quad (5)$$

where τ is the rotational correlation time for the radical in solution (T_2^{-1} is $2.8\pi\sqrt{3} \times 10^7 \Delta H$, with ΔH in millitesla. *N.B.*, in an earlier report,² the power of ten in this expression was wrongly transcribed).

For the 2,1,3-benzoselenadiazole radical anion in dimethoxyethane, the calculated contribution to ΔH from spin-rotation at 20°C (0.082 mT) leads to a value for τ of 0.6×10^{-12} s: at -80°C we find $\tau = 0.48 \times 10^{-11}$ s. By comparison, for the radical cation of phenoselenazine we found² the spin-rotation contribution to be *ca.* 0.030 mT (in nitroethane) at 20°C , giving $\tau = 2 \times 10^{-11}$ s. The longer correlation time for this than for (7) in dimethoxyethane at the same temperature must reflect the smaller size of the latter. However, we clearly cannot place much emphasis on the exactitude of these numbers (indeed the value for the 2,1,3-benzoselenadiazole anion we believe to be unrealistically small), but it is interesting that for radicals (1)–(3), which should have approximately the same correlation time under given

conditions, expression (5) accounts for the observation that a higher g -value is associated with more effective spin-rotational relaxation. Thus, equation (5) predicts contributions for (1), (2), and (3) in the order 19 : 2 : 7, which is at least in qualitative agreement with the order observed. The relationship between Δg and the spin density on selenium is discussed below.

From a qualitative viewpoint, one aspect of spin-rotational broadening appears puzzling. Since there appears to be a significant contribution to the line-width even for selenium-containing radicals with g *ca.* 2.007 and for which τ is *ca.* 10^{-11} s, we would expect even larger line-widths for small radicals like nitroxides and aliphatic nitro-radical-anions which have fairly high g -values (*ca.* 2.006) and, presumably, much shorter correlation times. This appears not to be the case, and we believe that the discrepancy arises from the oversimplification of assuming a single value of τ for each heterocyclic radical. Presumably these execute *anisotropic* rotational motion, with a relatively low frictional coefficient about the axis perpendicular to the molecular plane (see ref. 19); perhaps a relatively short rotational correlation time for this motion plays a dominant part in governing the line-width. It is interesting that spin-rotation interaction due to relatively free rotation about the long molecular axis has been suggested to account for the broad lines observed for some small radicals with a linear heavy atom framework, *e.g.*, $\cdot\text{CH}_2\text{C}\equiv\text{CH}$, $\cdot\text{CH}_2\text{C}\equiv\text{CCH}_3$,²⁰ $\cdot\text{CH}_2\text{-O}^-$,²¹ and $\cdot\text{CH}_2\text{CN}$.²²

Hyperfine splittings and molecular orbital calculations. Analysis and assignments of the e.s.r. spectra for radicals (1)–(7) are based on the results of Hückel and McLachlan calculations (see Table 1); ^1H , ^{14}N , and ^{77}Se splittings are all included. Only a p -orbital model for Se was explicitly considered.

For the phenoselenazine radical cation and nitroxide we have employed $h_{\text{N}} = 1.5$ and $k_{\text{CN}} = 1.0$, as suggested for some aromatic radical cations containing nitrogen²³ and for aromatic nitroxides.² For the neutral species we chose $h_{\text{N}} = 0.8$ and $k_{\text{CN}} = 1.0$, and we considered the same values appropriate for nitrogen in the diazole anion (see refs. 24 and 25). For the phenoxselenin cation we used $h_{\text{O}} = 2.0$ and $k_{\text{CO}} = 0.8$,²⁶ and for the selenium parameters we employed $h_{\text{Se}} = 1.21$, $k_{\text{CSe}} = 0.57$, and $k_{\text{NSe}} = 0.57$. The value of h_{Se} was obtained from the h_{O} and h_{S} used previously² by employing a scaling factor derived from 'representative values' of h for O, S, and Se given by other workers,⁷ k_{CSe} was set equal to k_{OS} since our earlier experience² suggested that sulphur- and selenium-containing radicals have closely similar spin-density distributions, and the value of k_{NSe} was chosen so as to give optimum agreement with calculated proton and nitrogen splittings in (7).

²⁰ H. G. Benson, A. J. Bowles, A. Hudson, and R. A. Jackson, *Mol. Phys.*, 1971, **20**, 713.

²¹ A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 786.

²² R. Livingston and H. Zeldes, *J. Magnetic Resonance*, 1969, **1**, 169.

²³ B. L. Barton and G. K. Fraenkel, *J. Chem. Phys.*, 1964, **41**, 1445.

²⁴ C. L. Talcott and R. J. Myers, *Mol. Phys.*, 1967, **12**, 549.

²⁵ A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, 1962, **5**, 21.

²⁶ A. Streitwieser, 'Molecular Orbital Theory for Organic Chemists, Wiley, New York, 1961, p. 135.

Predicted proton splittings were obtained for $\cdot\text{CH}$ fragments using the calculated $\rho^{\pi\text{O}}$ together with McConnell's equation, with $Q^{\text{H}_{\text{CH}}} = -2.70$ mT. For the radical (1) we chose $Q^{\text{N}} = 2.78$ mT and $Q^{\text{H}_{\text{NH}}} = -2.96$ mT, these being appropriate to our choice of $Q^{\text{H}_{\text{CH}}}$ (see refs. 2 and 23), for the neutral and nitroxide radicals we chose $Q^{\text{N}} = 1.65$ and 3.0 mT, respectively, and $Q^{\text{N}} = 2.58$ mT was used for the anion (*cf.* refs. 7 and 24). For the ^{77}Se splittings we have examined a simple proportionality relationship between a^{Se} and $\rho^{\pi\text{Se}}$, as suggested by our earlier results, rather than an expression involving spin density on adjacent atoms. The most successful account appears to be given by a value of Q^{Se} as the mean value of a^{Se} (expt.)/ $\rho^{\pi\text{Se}}$ (calc.) for the radicals (1)—(3) and (5): the values 12.3 mT (for McLachlan calculations) and 12.4 mT (for HMO calculations) result.

The assignments of observed proton splittings are made on the basis of these calculations and by comparison with results for sulphur-containing analogues. Then, inspection of the data for the radicals (1)—(3) and (5) indicates excellent agreement between the observed and calculated ^1H , ^{14}N , and ^{77}Se splittings. In particular, this approach gives a good account of the spin distribution in the three closely related radicals from phenoselenazine: thus, it can be seen that the calculations reproduce the decrease in π -spin density on selenium in the order (1) > (3) > (2) (as also indicated by the magnitudes of a^{Se} , the line-widths, and the g -values; see later). The calculations also reproduce, when considered together with those for the analogues of (1)—(3), the trends in each series when first S and then Se is substituted for O, as inferred from the experimental data: *i.e.*, the spin density on the heteroatom decreases in the order $\rho^{\pi\text{Se}} > \rho^{\pi\text{S}} > \rho^{\pi\text{O}}$. Further, the calculated values of $\rho^{\pi\text{Se}}$ for the radical cations (4) and (5) are in good agreement with those derived by Lamotte and Berthier⁴ from consideration of the g -values ($\rho^{\pi\text{Se}}$ values of 0.20 and 0.28, respectively, were estimated). For radicals (1)—(5), then, the calculations appear quite adequate and suggest that a planar p -orbital model is appropriate.

However, the calculations show some discrepancies for the radical-anions (6) and (7). Thus for (6), although the calculated proton hyperfine splittings are in good agreement with experiment, the selenium splitting is underestimated (though the absolute magnitude of the difference is not large; we were unable to determine the sign of a^{Se} from the spectra). The spin distribution appears to be quite close to that for the dibenzothiophen radical anion which has recently been discussed in some detail:²⁷ we agree with the signs and assignments for the latter, assuming only a small perturbation on going from sulphur to selenium. Since we have confidence in the calculated spin-density distribution (the very low g value and line-widths also confirm the very small spin density on selenium), we conclude that either the Q^{Se} value used above is inappropriate for anions or that in this type of radical, where the spin density on atoms flanking the

heteroatom is appreciable [in this case, 0.049 (HMO) or 0.044 (McLachlan)] it is inappropriate to account for a^{Se} simply in terms of a single Q value, since spin-polarisation from adjacent atoms may well be important. It occurs to us also to comment on the very low g -value (2.0030). It is conceivable that this near free-spin value may actually contain a negative contribution, such as might arise if the electron delocalisation in the radical incorporates some donation into empty d -orbitals on the heteroatom from the adjacent positions of higher spin density (see, *e.g.*, ref. 28).

In the radical anion (7), the calculated proton and nitrogen splittings are in good agreement with experiment, but the calculated selenium splittings are much greater than that observed (for which the sign could not be determined). It may be that the observed a^{Se} is lower than that predicted by the simple proportionality relationship because of the effect of the considerable spin-densities on adjacent atoms [0.242 (HMO) or 0.30 (McLachlan) on each nitrogen]. Again (see above) the g -value is not very high, it being considered that the spin density apparently resides almost exclusively on the two nitrogens and a selenium atom, and the possibility of negative contributions cannot be entirely ruled out.

We carried out extensive investigations for potential parameters which would enable us to reproduce both a^{H} and a^{Se} in (7) but with no further success. We feel that the extra parameters $Q^{\text{Se}_{\text{NSe}}}$ and $Q^{\text{Se}_{\text{CSe}}}$ for (6) and (7) are probably required in these cases, but we have insufficient information to determine these.

g-Values. As expected, the high g -values reflect the large spin-orbit coupling constant for selenium (1688 cm^{-1}) and they increase with increasing spin density (calculated) on the heteroatom.

Stone²⁹ has suggested a semiempirical theory to account for the g -values of aromatic radicals, to be used within the framework of the π -electron approximation and a minimum basis LCAO MO approach. This method expresses the isotropic g -shift, Δg^{iso} , for a radical as the sum (6) of contributions from each atom i in the molecule. The i th contribution can be written in terms

$$\Delta g^{\text{iso}} = \sum_i \Delta g_i \quad (6)$$

of c_i , the coefficient of the AO centred on i in the singly-occupied orbital ϕ , and λ , where the energy of the orbital ϕ is written $E = \alpha + \lambda\beta$, as in an HMO calculation. Thus, to first order in λ , we obtain equation (7) where a_i

$$\Delta g_i = (a_i + \lambda b_i)c_i^2 \quad (7)$$

and b_i are numerical constants (directly proportional to the spin-orbit coupling constant, ζ_i), characteristic of the type of atom, and determined experimentally. With the aid of HMO calculations and accurate experimental work on hydrocarbon anions and cations, Segal, Kaplan, and Fraenkel¹² have obtained values for carbon: $a_{\text{C}} =$

²⁷ F. C. Adam and C. R. Kepford, *Canad. J. Chem.*, 1971, **49**, 3529.

²⁸ T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 648.

²⁹ A. J. Stone, *Mol. Phys.*, 1966, **6**, 502.

TABLE 3

Estimated contribution to Δg (experimental) from spin-orbit coupling involving selenium ^a

Radical	λ (HMO)	c_{Se}^2	Δg_{Se}^{av} (calc.) ^b	Δg (exptl.)
Phenoselenazine radical cation	0.343	0.163	0.0103	0.0138
Phenoselenazine nitroxide	0.199	0.097	0.0055	0.0048
Phenoselenazine neutral radical	0.174	0.111	0.0062	0.0081
Dibenzodiselenin radical cation	0.495	0.207	(0.0290) ^c	0.0292
Phenoxselenin radical cation	0.506	0.238	0.0168	0.0205
Dibenzoselenophen radical anion	-0.750	0.016	(0.00024) ^c	0.0007
		0.063 ^d	0.0036 ^d	
2,1,3-Benzoselenadiazole radical anion	-0.116	0.179	0.0077	0.0039
		0.040 ^d	0.0017 ^d	

^a For method, see text. ^b Parameters employed: $a_{Se} = 0.0481$, $b_{Se} = 0.0448$. ^c Experimental values used to derive parameters. ^d Values derived from a^{Se} and Q^{Se} .

32×10^{-5} and $b_C = -17 \times 10^{-5}$. We have utilised these values in deriving appropriate values for selenium from our results. To do this, we have used expressions (6) and (7) for the two radicals containing only carbon and selenium atoms, *i.e.*, radicals (4) and (7), for which equation (8) applies. For radical (4), the HMO calcu-

$$\Delta g^{iso} = \sum_i c_i^2 (a_C + \lambda b_C) + \sum_j c_j^2 (a_{Se} + \lambda b_{Se}) \quad (8)$$

($i = C$) ($j = Se$)

lation gives $\lambda = 0.495$ and $\sum_i c_i^2 = 0.586$, and $\Delta g^{iso} = 0.0292$. For radical (6), we have $\lambda = -0.750$, $\sum_i c_i^2 = 0.983$, and $\Delta g^{iso} = 0.0007$. Applying equation (8) to

these, we derive $a_{Se} = 0.0481$ and $b_{Se} = 0.0448$. These values can now be used to estimate the contributions to the g -value (Δg_{Se}^{iso}) from spin on selenium in the radicals we have studied. The results are shown in Table 3 and they confirm the suggestion that the interaction with selenium plays a predominant part in governing the magnitude of g . For radicals (6) and (7) we have calculated Δg_{Se} using calculated c_i^2 values (HMO) and also from 'experimental' c_i^2 values (derived from Q^{Se} and a^{Se} ; see above). Agreement in these cases is rather poor, reflecting our uncertainty over a reliable estimate for ρ_{Se}^{π} where this is small and where adjacent atoms bear appreciable spin density.

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