Radical Cations and Anions of 1,2,4,5-Tetrazines: an Electron Spin Resonance and Cyclic Voltammetric Study

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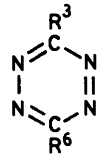
Exposure to ^{60}Co γ-rays of dilute solutions of a range of *s*-tetrazines in fluorotrichloromethane at 77 K gave the corresponding radical cations, identified by their e.s.r. spectra. Two distinct types of spectra were obtained, one showing large hyperfine coupling to four equivalent ^{14}N nuclei is assigned to *n*(σ)-radical cations, and the other, only found for $-NR_2$ substituents, with strong coupling to two nitrogen nuclei, is assigned to π-radical cations. The former include the parent *s*-tetrazine and the 3,6-dimethyl, -diphenyl, -dichloro, -dimethoxy, -bis(methylthio), and di(aziridin-1-yl) derivatives. The latter were also prepared in fluid solution, and showed reversible behaviour in their cyclic voltammograms, in contrast with the former group. The corresponding radical anions have been studied in both fluid and solid solution, all derivatives showing major hyperfine coupling to the four ring ^{14}N nuclei. Total spin densities have been estimated for both types of radical cations and for the radical anions, and in all cases the total is in the 1.05—1.2 range. This deviation from unity is interpreted in terms of spin polarisation giving rise to considerable negative spin densities.

In recent years various aromatic *N*-heterocycles (*e.g.* pyridine, diazines) have attracted particular interest due to the fact that the first lone-pair orbitals on nitrogen and the first π-orbitals are close in energy. Photoelectron (p.e.) spectroscopy gives direct information concerning the order of the lone-pair and π-ionisation potentials, provided the corresponding p.e. bands are resolved and can be unambiguously assigned to MO calculations. In case of band overlap the selection of the HOMO is rather arbitrary. This uncertainty can sometimes be solved by e.s.r. studies of the corresponding radical cations in solution. The recent discovery that various radical cations, not previously detected by e.s.r. spectroscopy, are readily generated by γ-irradiation of dilute solutions of the molecular precursors in Freon or other fluorinated solvents[1–5] has led to many successful studies of organic *n*(σ)-type radical cations. Such investigations confirmed that pyridine[6,7] and various diazines[1,8] form σ-radical cations on γ-irradiation at 70 K, in agreement with p.e. predictions.

When the orbital energies of the highest filled *n*(σ)- and π-orbital are very similar, appropriate substitution may change the order of these orbitals. This has been demonstrated in the pyridine series by alkyl substitution. For example, γ-irradiation of the 2,5-dimethyl derivative generated a π-radical cation.[7]

In this paper we report results of a similar study concerning 1,2,4,5-tetrazine (*s*-tetrazine) (**1a**) and its derivatives (**1b**—**m**). In the p.e. spectra of the primary compound (**1a**) and the 3,6-dimethyl derivative (**1b**) the first band was identified as the 'lone pair' band [*n*(σ)HOMO], the second as the π-band.[9] Substitution destabilises π-orbitals to a greater extent than *n*-orbitals with the effect that both bands shift to lower energies but overlap in the p.e. spectra of (**1f**—**h**) is extensive. Calculations suggest that the first band of (**1i**—**m**) should be assigned to a π-HOMO.[10] One aim of the present work was to check the p.e. results using e.s.r. studies of the corresponding radical cations (**1a**$^{+\bullet}$—**m**$^{+\bullet}$) and, in particular, to try to detect the switch in wavefunction from σ to π. Additional information on this point was expected to result from cyclic voltammetric experiments. Another aim was to compare the structures of the radical cations with those of the corresponding radical anions. Some preliminary results have already been published.[11]



(**1**) **a**; $R^3 = R^6 = H$
b; $R^3 = R^6 = Me$
c; $R^3 = R^6 = Ph$
d; $R^3 = R^6 = Cl$
e; $R^3 = R^6 = OMe$
f; $R^3 = R^6 = SMe$
g; $R^3 = R^6 = \overline{NCH_2CH_2}$
h; $R^3 = R^6 = NH_2$
i; $R^3 = R^6 = NHMe$
k; $R^3 = R^6 = NMe_2$
l; $R^3 = R^6 = \overline{NCH_2CH_2CH_2}$
m; $R^3 = R^6 = \overline{NCH_2CH_2CH_2CH_2}$

Results

Radical Cations.—Exposure of dilute solutions of the *s*-tetrazines (**1a**—**m**) in $CFCl_3$ to ^{60}Co γ-rays at 77 K led to the formation of two groups of radical cations (**1a**$^{+\bullet}$—**g**$^{+\bullet}$) and (**1k**$^{+\bullet}$—**m**$^{+\bullet}$). Typical spectra are illustrated in Figure 1. For the first group all spectra were almost identical, showing features of four equivalent ^{14}N nuclei with a maximum separation of ~30 G and a minimum separation of ~19 G. The resulting e.s.r. parameters are given in Table 1(i). The second group of radical cations (**1k**$^{+\bullet}$—**m**$^{+\bullet}$) gave quite different e.s.r. spectra, showing large hyperfine couplings to two equivalent ^{14}N nuclei and twelve equivalent (**1k**$^{+\bullet}$) or eight equivalent protons (**1l**$^{+\bullet}$) and (**1m**$^{+\bullet}$). In these radical cations the SOMO is π, being strongly localised on the two amino nitrogen atoms. The connecting *s*-tetrazine system can be regarded as a conjugated spacer between the two nitrogen centres. The latter radical cations are more persistent than the representatives of the first group and it was possible to record highly resolved liquid-phase spectra.

The species (**1k**$^{+\bullet}$—**m**$^{+\bullet}$) were generated by oxidation of the parent *s*-tetrazines in trifluoroacetic acid–trifluoroacetic acid anhydride (9:1) with 3-chloroperbenzoic acid. In agreement with the matrix results the liquid-phase e.s.r. spectra yield large hyperfine coupling constants for the two amino nitrogen nuclei and their β-protons. The ^{14}N nuclei of the *s*-tetrazine ring show only small splittings. For example, the e.s.r. spectrum of (**1k**$^{+\bullet}$) gives a(H) = 8.75 (12H), a(N) = 8.09 (2N), and a(N) = 1.17 G (4N). Even larger H(β) hyperfine coupling constants were observed for the azetidine (**1l**$^{+\bullet}$) and the pyrrolidine (**1m**$^{+\bullet}$) derivatives due to the smaller dihedral angle θ between the nitrogen π-orbital and the β-hydrogen–carbon bond. The e.s.r. spectrum of (**1l**$^{+\bullet}$) is shown in Figure 2. This species additionally exhibits small splittings of the γ-protons in R. The g_{av}-values are found to be about 2.0045. The isotropic e.s.r. data of (**1k**$^{+\bullet}$—**m**$^{+\bullet}$) are given in Table 2(i).

However, the order of persistency (**1k**$^{+\bullet}$) ≫ (**1l**$^{+\bullet}$) > (**1m**$^{+\bullet}$) does not follow the magnitudes of the half-wave oxidation potentials (Table 2). Furthermore, all attempts to detect radical cations of the remaining *s*-tetrazines with $-NR_2$ substituents (**1g**—**i**) by e.s.r. spectroscopy in the liquid phase were not successful.

Radical Anions.—Various *s*-tetrazines yield persistent radical anions by electrolytic reduction, *e.g.* (**1a**$^{-\bullet}$),[12] by disproportionation in deoxygenated solvents containing a strong base, *e.g.*

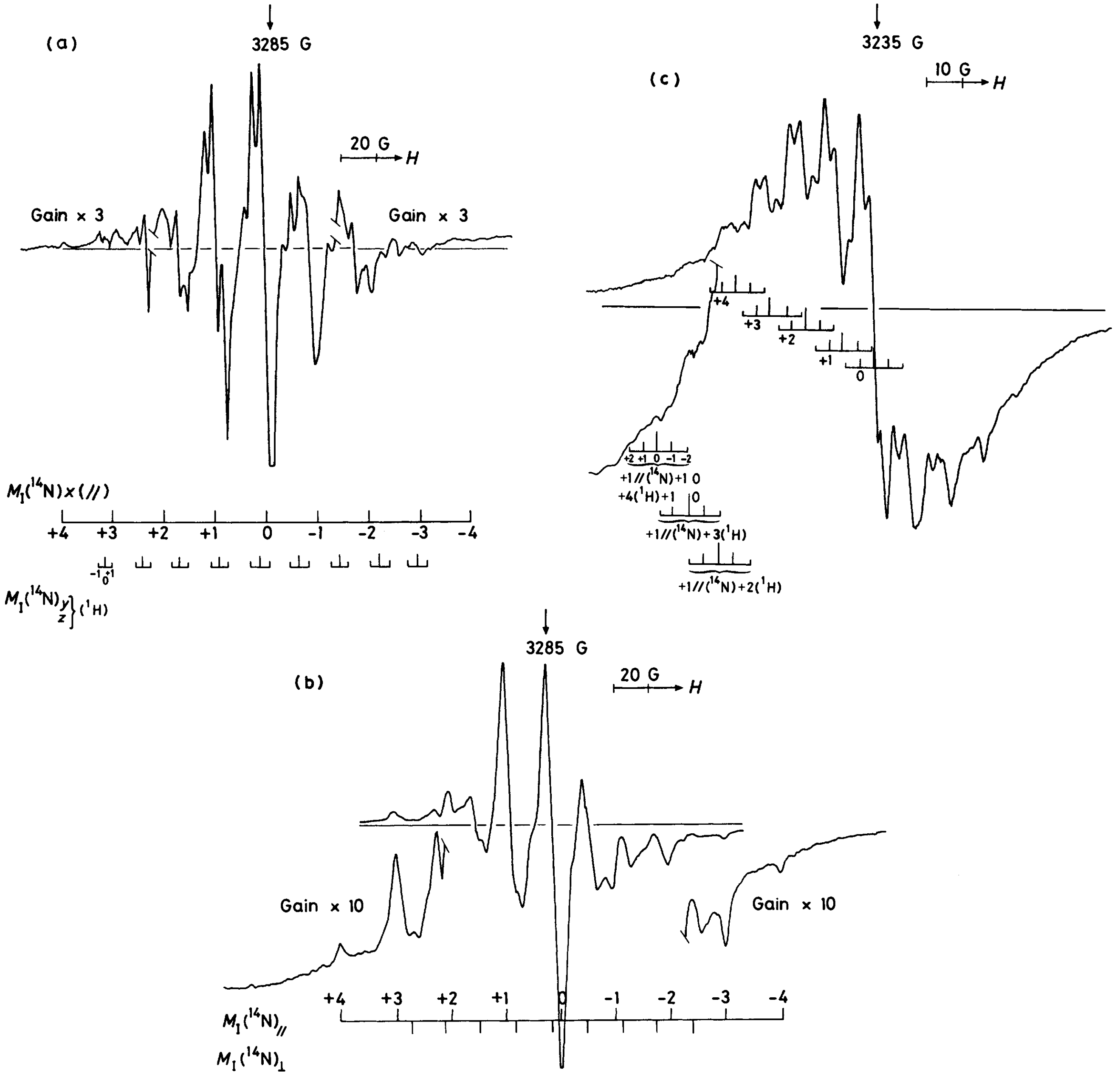


Figure 1. First-derivative X-band e.s.r. spectra for a range of *s*-tetrazines in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the corresponding radical cations: (a) *s*-tetrazine (**1a**$^{+\bullet}$), (b) the bis(methylthio) derivative (**1f**$^{+\bullet}$), and (c) the bis(dimethylamino) derivative (**1k**$^{+\bullet}$)

Table 1. ^{14}N and ^{1}H hyperfine coupling constants for *s*-tetrazine radical cations in $CFCl_3$ at 77 K together with derived orbital populations (%); (i) *n*(σ)-type, (ii) π-type

	$R^3 = R^6$	N_i	$A_{\parallel}/G^a$	$A_{\perp}/G^a$	A_{iso}/G^a	$2B$	a_s^2	a_p^2
(i) (**1a**$^{+\bullet}$)	H	4 N	29.1	21	23.7	5.4	4.3	16
		2 H	~4	0	~1.3			
(**1b**$^{+\bullet}$)	Me	4 N	29	20	23	6.0	4.1	18
(**1c**$^{+\bullet}$)	Ph	4 N	30	18	22	8.0	4.0	24
(**1d**$^{+\bullet}$)	Cl	4 N	31.5	16.5	21.5	10.0	3.9	30
(**1e**$^{+\bullet}$)	OMe	4 N	30	18.5	22.3	7.7	4.0	23
(**1f**$^{+\bullet}$)	SMe	4 N	32	20	24	8.0	4.3	24
(**1g**$^{+\bullet}$)	$\overline{NCH_2CH_2}$	4 N	29	17.6	21.4	7.6	3.9	23
(ii) (**1k**$^{+\bullet}$)	NMe_2	2 N	~22	~0	8.09^b	~13.9	1.5	42
		4 N	~3.5	~0	~1.2			
		12 H			~10			
(**1l**$^{+\bullet}$)	$\overline{NCH_2CH_2CH_2}$	2 N	*c*	~0	8.14^b			
		8 H			14.3			
(**1m**$^{+\bullet}$)	$\overline{NCH_2CH_2CH_2CH_2}$	2 N	*c*	~0				
		4 H			~17.5			
		4 H			~8			

^{a} 1 G = 10^{-4} T. ^{b} Liquid-phase result. ^{c} ±1 Features not resolved.

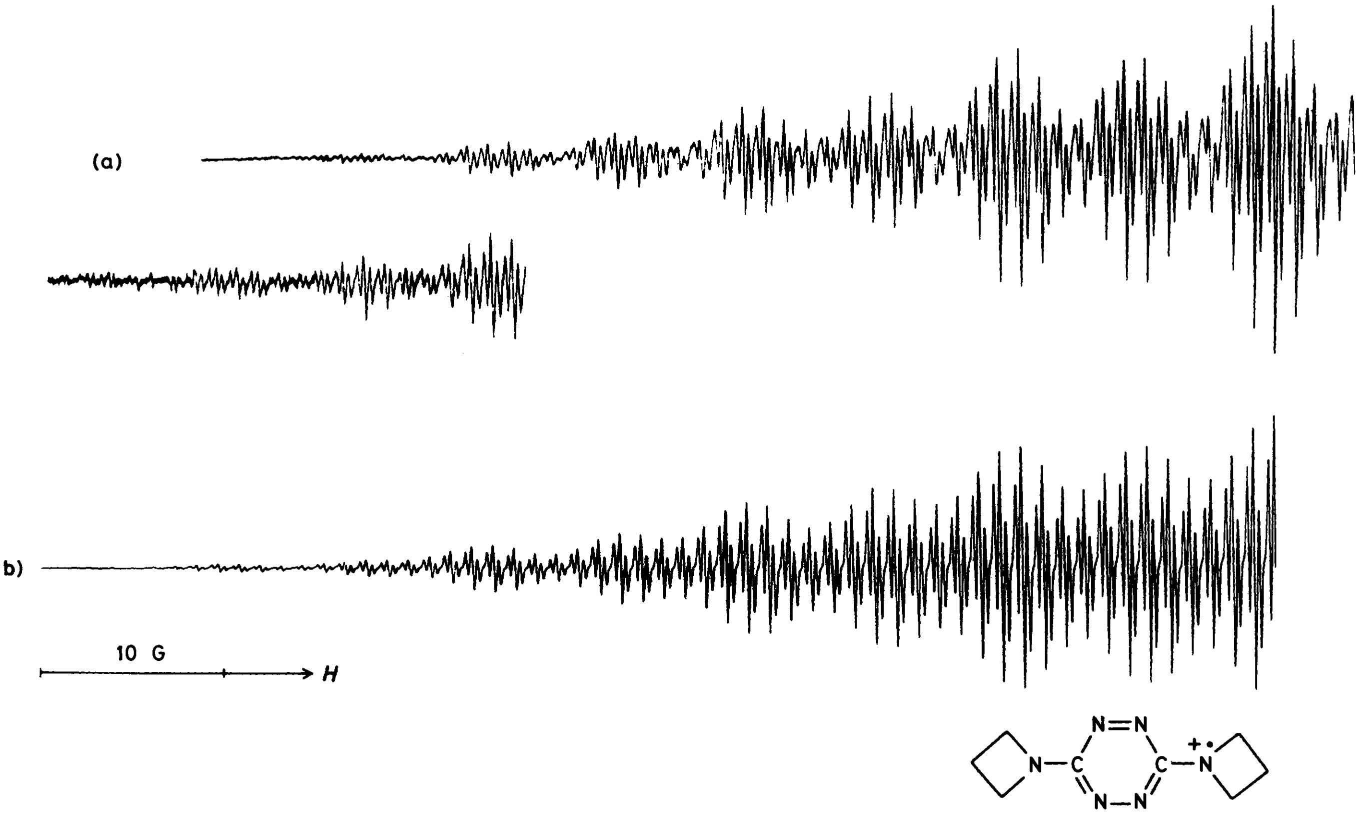


Figure 2. (a) First-derivative X-band e.s.r. spectrum for the radical cation of the di(azetidin-1-yl) derivative (**1l**$^{+\bullet}$) in [CF_3CO_2H–$(CF_3CO)_2O$ (9:1)] at 293 K together with (b) a simulation using the data in Table 2(i). Only the low-field halves of the spectra are shown

(**1b**$^{-\bullet}$),[13–15] or by using the enolate anion of propiophenone as a one-electron reducing agent,[16,17] *e.g.* (**1h**$^{-\bullet}$).[18] In this study, (**1g**$^{-\bullet}$—**k**$^{-\bullet}$) were generated electrolytically (0.1M-tetrabutylammonium perchlorate), (**1l**$^{-\bullet}$) and (**1m**$^{-\bullet}$) were obtained by reduction with propiophenone enolate anion, and (**1b**$^{-\bullet}$), (**1c**$^{-\bullet}$), (**1e**$^{-\bullet}$), and (**1f**$^{-\bullet}$) were formed spontaneously by disproportionation when dissolved in dimethyl sulphoxide (DMSO) containing potassium t-butoxide.

The isotropic hyperfine coupling constants of (**1a**$^{-\bullet}$—**m**$^{-\bullet}$) in DMSO are given in Table 2(ii). The e.s.r. spectra of all radical anions show nine lines or groups of lines separated by about 5.2 G, a pattern consistent with four equivalent nitrogen atoms. Examples of these spectra are illustrated in Figures 3 and 4(a). Small splittings from nuclei of the various R substituents were also observed, including, in one case, from protons in the γ-position. All radical anions yielded g_{av}-values of 2.0041 which are slightly smaller than those of the corresponding π-radical cations.

Table 2. Isotropic hyperfine coupling constants for (i) various radical cations in trifluoroacetic acid–trifluoroacetic acid anhydride (9:1) and (ii) radical anions in dimethyl sulphoxide (DMSO) at 293 K together with their half-wave oxidation and reduction potentials in acetonitrile

	$R^3 = R^6$	$a(N)$/G	$a(i,R)$/G	g-Value	$E_{\frac{1}{2}}$/V[a]
(i) (**1k**$^{+\bullet}$)	NMe_2	1.17 (4 N)	8.09 (2 N) 8.75 (12 H)	2.0046	+0.71
(**1l**$^{+\bullet}$)	$NCH_2CH_2CH_2$	1.16 (4 N)	8.14 (2 N) 13.95 (8 H) 0.32 (4 H)	2.0044	+0.75
(**1m**$^{+\bullet}$)	$NCH_2CH_2CH_2CH_2$	1.12 (4 H)	8.00 (2 N) 12.80 (8 H) 0.22 (8 H)	2.0045	+0.66
(ii) (**1a**$^{-\bullet}$)	H	5.275 (4 N)[b]	0.212 (2 H)[b]	2.0041	−1.16 (−1.20)[c]
(**1b**$^{-\bullet}$)	Me	5.13 (4 N)	1.54 (6 H)	2.0041	−1.32 (−1.36)[c]
(**1c**$^{-\bullet}$)	Ph	5.06 (4 N)	0.17 (6 H)[d]	2.0040	−1.21 (−1.24)[c]
(**1d**$^{-\bullet}$)	Cl				−0.56
(**1e**$^{-\bullet}$)	OMe	5.29 (4 N)[e]		2.0041	−1.13
(**1f**$^{-\bullet}$)	SMe	5.34 (4 N)		2.0041	−1.03
(**1g**$^{-\bullet}$)	NCH_2CH_2	5.25 (4 N)	0.91 (2 N) 0.23 (8 H)	2.0041	−1.25
(**1h**$^{-\bullet}$)	NH_2	5.22 (4 N)	0.72 (2 N, 4 H)	2.0041	
(**1i**$^{-\bullet}$)	NHMe	5.22 (4 N)	0.70 (2 N) 0.46 (2 H)	2.0041	−1.51
(**1k**$^{-\bullet}$)	NMe_2	5.21 (4 N)	0.69 (2 N)	2.0041	−1.55
(**1l**$^{-\bullet}$)	$NCH_2CH_2CH_2$	5.29 (4 N)	0.79 (2 N)	2.0041	−1.47
(**1m**$^{-\bullet}$)	$NCH_2CH_2CH_2CH_2$	5.22 (4 N)	0.66 (2 N)	2.0041	−1.60

[a] $E_{\frac{1}{2}}$-Values corrected relative to ferrocene, $E_{\frac{1}{2}} = 0.0906$ V. [b] Ref. 12. [c] Ref. 21. [d] 2′,4′,6′-Protons. [e] Ref. 23.

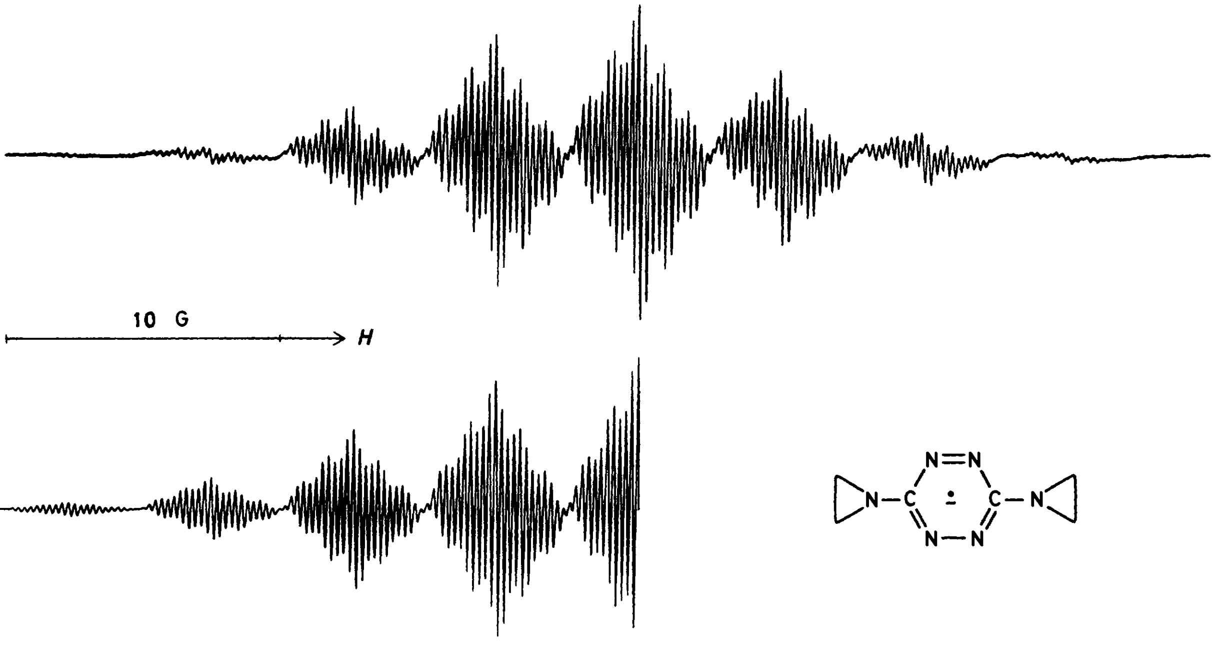


Figure 3. (a) First-derivative X-band e.s.r. spectrum for the radical anion of the di(aziridin-1-yl) derivative (**1g**$^{-\bullet}$) in dimethyl sulphoxide at 293 K together with (b) a simulation using the data in Table 2(ii)

We have also prepared these radical anions in glassy matrices by the use of ionising radiation. Although resolution is poor, it was possible to extract the anisotropic hyperfine parameters in several cases, using CD_3OD as a matrix. A typical example of these spectra is shown for (**1f**$^{-\bullet}$) in Figure 4. As is generally found for powder spectra of nitrogen-centred π-radicals the ^{14}N parallel coupling is readily measured. The ^{14}N perpendicular splitting is too small to be resolved but can be estimated from $A_{\parallel}(^{14}N)$ and the values of $A_{iso}(^{14}N)$ observed in the solution spectrum at 293 K. This gives $A_{\perp} \leq 1$ G in all cases.

Electrochemical Measurements.—Reduction potentials of (**1a**) have been reported in the literature.[12,19–21] A number of differently substituted *s*-tetrazines have been reduced electrochemically, and the resulting half-wave reduction potentials, $E_{\frac{1}{2}}$, of 3,6-diaryl-substituted *s*-tetrazines have been correlated with Hammett σ-constants.[21] We have carried out cyclic voltammetric measurements of the *s*-tetrazines (**1a**—**m**), except the insoluble diamino derivative (**1h**), in order to obtain a quantitative measure of the relative HOMO and LUMO energies in solution.

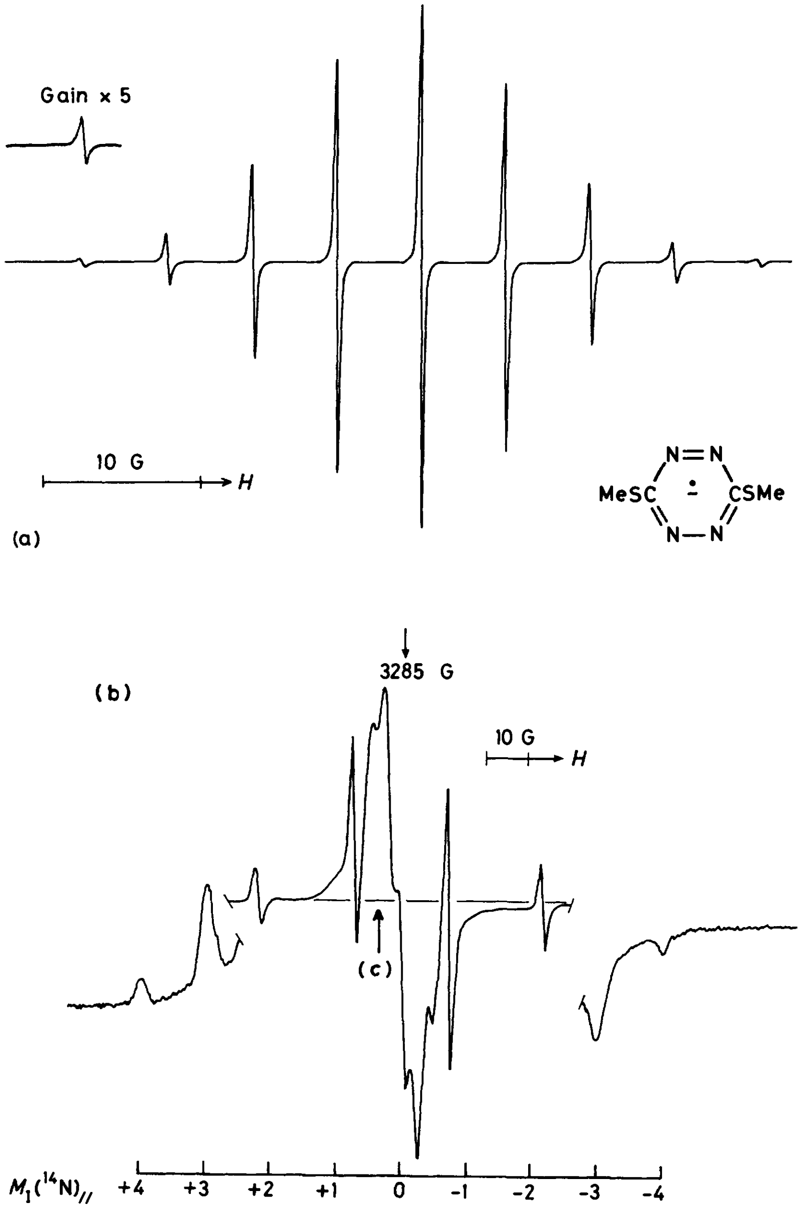


Figure 4. First-derivative X-band e.s.r. spectra for the radical anion of the bis(methylthio) derivative (**1f**$^{-\bullet}$): (a) in dimethyl sulphoxide at 293 K, and (b) in CD_3OD formed by exposure to ^{60}Co γ-rays at 77 K. The parallel features are indicated by the stick diagram. Features for methyl radicals are also shown. The central feature (c) is a mixture of the isotropic $|0\rangle$ lines for the anion together with solvent radicals (mainly $D^2\dot{C}OH$)

Provided the half-wave oxidation potential $E_{\frac{1}{2}}$ refers to a reversible process, solution-phase $E_{\frac{1}{2}}$ values can be correlated with vapour-phase ionisation potentials. Excellent linear correlations have been found for a wide range of compounds.[22] In our series only the cyclic voltammograms of three *s*-tetrazines (**1k**—**m**) exhibit a clean reversible one-electron oxidation process, an example being shown in Figure 5(a). The wave slope of about 60—70 mV indicates a kinetically uncomplicated, diffusion-controlled oxidation to the corresponding radical cations. The values of the half-wave oxidation potentials $E_{\frac{1}{2}}$, +0.71 (**1k**), +0.75 (**1l**), and +0.66 (**1m**), reflect exactly the order of the first p.e. ionisation potentials which correspond to the ejection of an electron from the highest occupied π-orbital of these compounds [Figure 5(b)].[10] All the other *s*-tetrazines show, in their cyclic voltammograms, either no oxidation or an irreversible oxidation process under the experimental conditions applied.

Owing to the strong electron-acceptor property of the *s*-tetrazine ring, these compounds are easily reduced to stable radical anions. In agreement with published results,[21] the cyclovoltammograms of all studied *s*-tetrazines (**1a**—**m**) yield a clean reversible redox couple with peak separations of about 60—70 mV. The measured half-wave reduction potentials are included in Table 2. The $E_{\frac{1}{2}}$ values of (**1a**—**c**) agree well with published data.[21]

Discussion

Radical Cations.—The structure of various *s*-tetrazines are remarkably constant with respect to the ring bond lengths and angles, average values being included in Figure 6.[24—27]

However, the exocyclic bonds of the $(–OMe)_2$ and $(–NR_2)_2$ derivatives are very short indicating considerable π-bonding [(**1e**)[26] C–OMe 1.328 Å, (**1g**) C–$\overline{NCH_2CH_2}$ 1.385 Å, and (**1h**)[27]

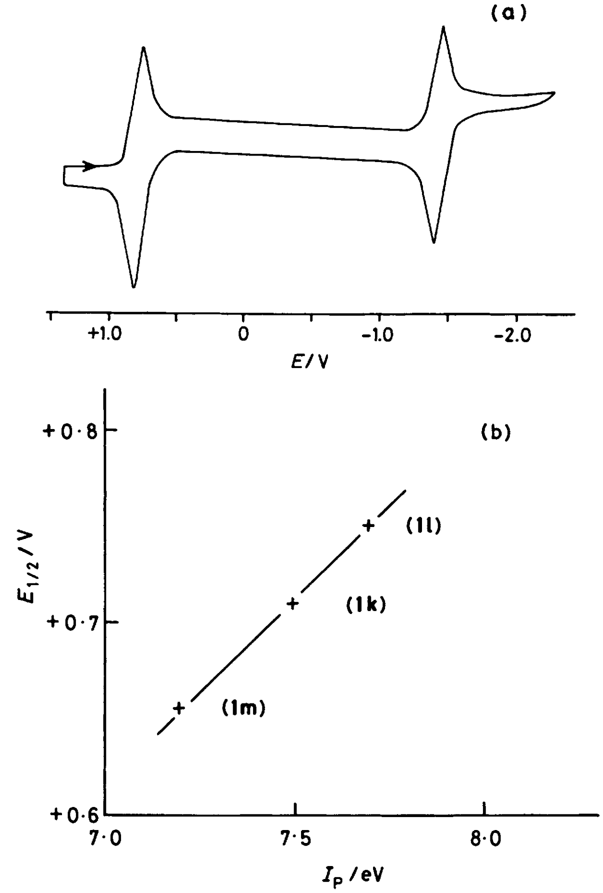


Figure 5. (a) Cyclic voltammogram of (**1l**) in acetonitrile. (b) Plot of half-wave oxidation potentials $E_{\frac{1}{2}}$ *versus* first p.e. ionisation potentials for (**1k**—**m**)[10]

C–NH_2 1.322 Å]. This is expected in view of the high effective electron affinity of the ring, and the π-donor ability of these substituents. It is this effect which raises the uppermost π level towards or even above that of the σ(*n*) level, which is the HOMO for the parent compound.

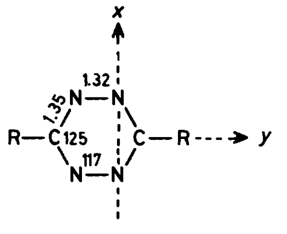


Figure 6.

The two quite distinct sets of e.s.r. spectra obtained from the radical cations in $CFCl_3$ are in good accord with these considerations, the change for σ(*n*) to π occurring on going from OR to NR_2 substituents. The bis(methylthio) derivative falls into the σ(*n*) group, together, perhaps surprisingly, with the di(aziridin-1-yl) derivative. That the latter should differ from the other nitrogen substituents accords with the low π-donor ability of the aziridin-1-yl group. Angular constriction together with electronic factors results in a rigid pyramidal structure at the nitrogen. This pyramidal structure persists to a large extent even if the electron lone pair in a *n*-orbital highly localised on nitrogen interacts with an adjacent strong electron acceptor such as the *s*-tetrazine π-system, as shown by the *X*-ray structure analysis.[26] This anomaly of the di(aziridin-1-yl) derivative is reflected in the cyclic voltammogram, where no reversible oxidation is observed under the experimental conditions applied, and in the inability to obtain liquid-phase e.s.r. spectra for the radical cation.

The ^{14}N hyperfine data for the *n*(σ) cations have been converted into isotropic (*A*) and anisotropic (2*B*) components on the assumption that $A_{\parallel}$ and $A_{\perp}$ are positive, and hence orbital populations for the 2*s* and 2*p* orbitals on nitrogen have been estimated in the usual way.[28] These values, included in Table 1, show that the total spin density on the four nitrogen atoms is always close to, but slightly greater than, unity (1.04—1.12). We do not attach great significance to this deviation from unity, it probably arises because of spin polarisation, giving rise to negative spin densities. The results do justify our assumption that experimental $A_{\text{max.}}(^{14}N)$ values are close to the true $A_{\parallel}$ values. This implies that the principal axes for the 4 component orbitals of the SOMO are close to being parallel to one another, all lying close to the *x* axis (Figure 6). Also, had these individual axes differed greatly from *x* the resulting spectra would have shown extra splittings which were not observed. The $a_p^2:a_s^2$ ratios of *ca.* 5.5 are a measure of the extent of hybridisation of these local orbitals. This value can be compared with that estimated for pyridine radical cations (8.3),[6,7] pyridazine radical cations (3.5), and pyrazine radical cations (7.2).[1,8] Results for pyrimidine radical cations are controversial,[1,8] but if the localised model is accepted, they are close to that for pyridine radical cations.

Clearly, in all cases mentioned, the SOMO comprises a linear combination of the 'lone pair' orbitals on the four nitrogen atoms. This is the SOMO predicted from calculations and verified by p.e. studies for the primary compound (**1a**) and the 3,6-dimethyl derivative (**1b**).[8] In the p.e. spectra of (**1f**) and (**1g**) due to the band overlap there was some uncertainty regarding the selection of the HOMO.[10] The e.s.r. spectra of ($\mathbf{1f}^{+\bullet}$) and ($\mathbf{1g}^{+\bullet}$) clearly prove that the SOMO is of σ(*n*)-type. In agreement with these results the cyclic voltammograms of (**1a**—**g**) show no or an irreversible oxidation under the experimental conditions applied. We stress that there is no requirement for an exact link between the p.e.s. results and e.s.r. results since the former are governed by the Franck–Condon principle whilst the latter relate to relaxed cations.

The switch in wavefunction lies between (**1f**), (**1g**), and (**1i**) (R^3 = R^6 = SMe, $\overline{NCH_2CH_2}$, and NHMe, respectively). The -NR_2-substituted *s*-tetrazines (**1k**—**m**) show in their cyclic voltammograms a clean reversible one-electron oxidation to the corresponding radical cations, and the determined half-wave oxidation potentials [Table 2(i)] follow the order of the first p.e. ionisation potentials of these compounds [*cf.* Figure 5(b)], assigned to the highest occupied π-orbital.[10] The radical cations of the second group are more persistent than those of the first series. There has been no problem in obtaining highly resolved liquid-phase e.s.r. spectra for ($\mathbf{1k}^{+\bullet}$—$\mathbf{m}^{+\bullet}$). The results show that these radical cations have a π-SOMO strongly localised on the two exocyclic nitrogen atoms.

As can be seen from Figure 1(a) the spectrum for ($\mathbf{1a}^{+\bullet}$) (*H*) is more complex than any of the other σ-radical cations such as ($\mathbf{1e}^{+\bullet}$) (OMe) shown in ref. 11 or ($\mathbf{1f}^{+\bullet}$) (SMe) shown in Figure 1(b). This is because there is a resolved triplet splitting assignable to the two C–H protons. However, this only appears on one set of features (*z*). Clearly this cannot be assigned to electron delocalisation onto the proton, since this would give a major isotropic component. A consideration of the dipolar coupling for *ca.* 50% of the electron divided between the two adjacent nitrogen atoms show that for in-plane fields coupling from one site tends to cancel that from the other so that the net effect is small. However, when *H* is normal to the plane, the effects combine, and a splitting of *ca.* 4 G becomes reasonable.

Table 3. ^{14}N And ^{1}H hyperfine coupling constants for *s*-tetrazine radical anions in CD_3OD at 77 K together with derived orbital populations (%)

	$R^3 = R^6$	N_i	$A_{\parallel}/G$	$A_{\perp}/G$	A_{iso}[a]	$2B$[b]	a_p^2[c]
($1a^{-\cdot}$)	H	4 N	15.2	~0	5.1	9.9	30
		2 H	~2.0				
($1b^{-\cdot}$)	Me	4 N	15.0	~0	5.0	9.9	30
		6 H	~2.0				
($1c^{-\cdot}$)	Ph	4 N	~14	~0	4.7	8.9	27
($1d^{-\cdot}$)	Cl	4 N	15.5	~0	5.2	~10.3	31
($1e^{-\cdot}$)	OMe	4 N	15.3	~0	5.1	10.0	30
($1f^{-\cdot}$)	SMe	4 N	15.5	~0	5.2	10.2	31
($1h^{-\cdot}$)	$NH_2(ND_2)$	4 N	15.3	~0	5.1	10.1	30
($1i^{-\cdot}$)	NHMe(NDMe)	4 N	15.3	~0	5.1	10.1	30

[a] Calculated using $A_{\perp} = 0$. [b] Calculated using A_{iso} for solution when known. [c] a_s^2 ~0.95%.

We conclude that there is no significant direct delocalisation into the C–H σ-orbitals, as required by the SOMO which has a nodal plane through the HC----CH units, and that the observed splitting is largely dipolar in character.

In contrast with the C–H orbitals, the in-plane *p*-orbitals of the chlorine substituents are expected to participate in the SOMO. However, no coupling to ^{35}Cl or ^{37}Cl nuclei could be detected, although the parallel features were somewhat broadened.

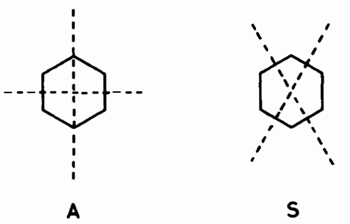
The solid-state spectra for the π-radical cations were well defined for the $|0>$ (^{14}N) lines but the parallel (±1) lines were very poorly resolved [*cf.* Figure 1(c)]. For the bis(dimethylamino) ($-N_2$) derivative extra splittings were observed which we attribute to the parallel coupling for the four ring ^{14}N nuclei. The value of *ca.* 4 G accords well with the isotropic coupling of 1.17 G, giving $A_{\perp} \approx 0$, as expected for the π-radical cations. Hence, from the solid-state data we can again obtain an approximate value of the total spin density. This gives *ca.* 0.84 on the amino nitrogen atoms and 0.28 on the ring nitrogen atoms, the total of 1.12 is again considerably greater than unity, in accord with expected negative spin density contributions.

This result ignores the hyperconjugative delocalisation involving the β-C–H bonds of the amino substituents, which is quite extensive, as judged from the ^{1}H coupling constants. It is noteworthy that for the di(aziridin-1-yl) derivative all the β-protons remain identical at 77 K, whilst for the five-membered-ring substituents they split into two sets of four equivalent protons (A_H = 17.5 and 8 G), the average being close to the liquid-phase value (12.8 G). Thus ring 'inversion' remains fast for the four-membered ring but is slow on the e.s.r. time scale at 77 K for the five-membered ring. The approximate factor of 2 between 'axial' and 'equatorial' protons reflects that found for the corresponding amino radical cations.

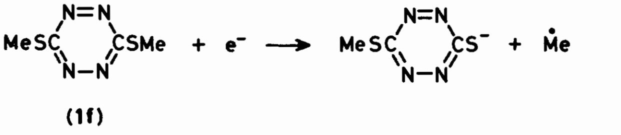
Radical Anions.—Radical anions of several *s*-tetrazines have already been previously studied in the liquid phase, *e.g.* ($1a^{-\cdot}$),[12] ($1b^{-\cdot}$),[13–15] ($1c^{-\cdot}$),[18] ($1e^{-\cdot}$),[23] and ($1h^{-\cdot}$).[18] Also various new radical anions, listed in Table 2(ii), have been generated and studied by e.s.r. All e.s.r. spectra are characterised by nine lines or groups of lines, separated by about 5.2 G, due to hyperfine coupling to four ^{14}N nuclei [Figure 4(a)]. As predicted by McLachlan calculations of ($1b^{-\cdot}$)[13] and *ab initio* studies of ($1a^{-\cdot}$)[29] the π-SOMO is confined to the four ring nitrogen atoms with some negative spin densities on the ring carbons.

We have now obtained spectra of these radical anions in glassy matrices by use of ionising radiation. Methanol (CD_3OD) was selected since anions are usually the only product formed by solutes in this matrix. Only the ^{14}N parallel coupling could be clearly detected. The perpendicular feature was not resolved ($A_{\perp}$ ~0 G) [Figure 4(b)]. By using A_{iso} from the liquid-phase e.s.r. spectra the purely anisotropic part of the hyperfine tensors ($2B$) can be estimated. The derived $2p$ orbital populations confirm a clear π-SOMO and yield a total spin density of *ca.* 1.2 in agreement with the liquid-phase results. This result confirms the theoretical prediction of negative spin density.

For radical anions of benzene derivatives it is usually found that there is considerable mixing of the two π-orbitals A and S that are formally degenerate for the parent benzene radical anion. The remarkable similarity in the ^{14}N parameters for the *s*-tetrazine radical anions suggest that, in general, only the A-type orbitals are involved. However, for the 3,6-diphenyl derivative ($1c^{-\cdot}$), $A_{\parallel}(^{14}N)$ is considerably reduced (Table 3) and, although no ^{1}H coupling was resolved, the parallel features were broader than for the other anions, which may have been caused by unresolved proton coupling. The data suggest *ca.* 10% admixture of the S-type orbital.



One interesting result of the electron-capture studies is that, for the bis(methylthio) derivative ($1f^{-\cdot}$), methyl radicals were formed in addition to the radical anions [Figure 4(b)]. Presumably the dissociative electron-capture reaction (1) occurred prior to relaxation of the anion, since no further generation of methyl radicals from the radical anions was observed on annealing.



(1)

(1f)

In contrast, methyl radicals were only just detectable in the spectra of the bis(methoxy) derivative ($1e^{-\cdot}$), so that the reaction corresponding to (1) is clearly far less favourable in this case.

Experimental

^{1}H N.m.r. spectra were obtained with a Bruker WP 80 instrument for [$^{2}H_6$]dimethyl sulphoxide solutions at room temperature, with tetramethylsilane as internal standard. Mass spectra were taken on a Dupont CEC 21-492.

E.s.r. spectra of the π-radicals at 293 K were measured with a Varian V-4500 spectrometer; *g*-values were determined by using an AEG n.m.r. gaussmeter and the Hewlett-Packard frequency converter 5246 L (calibration with perylene radical cation).

Samples were γ-irradiated at 77 K in a Vickrad ^{60}Co γ-ray source at a dose rate of *ca.* 0.8 Mrad h^{-1} for up to 1 h. E.s.r. spectra were recorded directly after exposure at 77 K on a Varian E-109 spectrometer. Samples were annealed to the melting points of the solvents, but no significant secondary products were detected prior to loss of signal.

Cyclic voltammetry studies were carried out on deoxygenated acetonitrile[30] solutions containing the *s*-tetrazine sample (0.4—0.8 mM) and tetraethylammonium tetrafluoroborate (0.1M)[21] at 298 K. The cyclic voltammograms of these solutions were obtained using a Bruker Universal Modular Polarograph E 310 attached to an electrochemical cell which consisted of a 'Glassy Carbon Electrode' as working electrode, a standard Ag/Ag^+ reference electrode, and a platinum counter electrode. Cyclic voltammograms were scanned at a current of 0.1—0.5 mA and a sweep rate of about 100 mV s^{-1}. $E_{\frac{1}{2}}$-Values are corrected relative to ferrocene, $E_{\frac{1}{2}} = 0.0906$ V.

Compounds **(1a)**,[31] **(1b)**,[32] **(1c)**,[33] **(1d)**,[34] **(1e)**,[23] **(1f)**,[35] **(1h)**,[36] and **(1k)**[37,38] were prepared as described in the literature; compounds **(1i)**, **(1g)**, **(1l)**, and **(1m)** were synthesised following a known method.[37]

3,6-*Bis*(*methylamino*)-1,2,4,5-*tetrazine* **(1i)**.—Compound **(1f)** (1.74 g, 10 mmol) and methylamine (10 ml, ~0.2 mol) in a sealed glass tube reacted for 1 d at room temperature. On evaporation of the methylamine the residue was crystallised from methanol to give red crystals, **(1i)** (870 mg, 62%), m.p. 184—185 °C (Found: C, 34.45; H, 5.85; N, 60.05. $C_4H_8N_6$ requires C, 34.28; H, 5.75; N, 59.97%); δ 2.86 (6 H, d, *J* 4.9 Hz, Me) and 7.26 (2 H, q, NH); *m*/*z* 140 (M^+, 100%).

3-(*Aziridin*-1-*yl*)-6-*methylthio*-1,2,4,5-*tetrazine and* 3,6-*Di*-(*aziridin*-1-yl)-1,2,4,5-*tetrazine* **(1g)**.—Compound **(1f)** (1.74 g, 10 mmol) in aziridine (1.08 g, 25 mmol) was stirred at room temperature for 2—3 h. The mixture was then evaporated under reduced pressure and the residue chromatographed on Merck silica gel using ethyl acetate as eluant. The first main red fraction was collected, evaporated under reduced pressure, and the residue recrystallised from methanol to give 3-(*aziridin*-1-*yl*)-6-*methylthio*-1,2,4,5-*tetrazine* (700 mg, 41%) as red needles, m.p. 68—69 °C (Found: C, 35.80; H, 4.20; N, 41.15. $C_5H_7N_5S$ requires C, 35.49; H, 4.17; N, 41.39%); δ 2.58 (4 H, s, CH_2) and 2.69 (3 H, s, Me); *m*/*z* 169 (M^+, 100%).

Further elution gave **(1g)** (260 mg, 16%) as orange crystals from methanol, m.p. 206 °C (decomp.) (Found: C, 43.85; H, 4.70; N, 5.10. $C_6H_8N_6$ requires C, 43.90; H, 4.91; N, 51.19%); δ 2.53 (s); *m*/*z* 164 (M^+, 100%).

3-(*Azetidin*-1-*yl*)-6-*methylthio*-1,2,4,5-*tetrazine and* 3,6-*Di*-(*azetidin*-1-*yl*)-1,2,4,5-*tetrazine* **(1l)**.—Compound **(1f)** (1.74 g, 10 mmol) and azetidine (1.43 g, 25 mmol) in a sealed glass tube were heated for 8—10 h at 120 °C. On cooling the mixture was treated with water and the product extracted into diethyl ether. The ethereal solution was washed with water, dried, and evaporated under reduced pressure. The red-brown residue was chromatographed on Merck silica gel using ethyl acetate as eluant. The first red fraction gave 3-(*azetidin*-1-*yl*)-6-*methylthio*-1,2,4,5-*tetrazine* (115 mg, 6%), as red crystals from ethanol, m.p. 81—82 °C (Found: C, 39.40; H, 5.00; N, 38.40. $C_6H_9N_5S$ requires C, 39.33; H, 4.95; N, 38.22%); δ 2.48 (2 H, quin, *J* 7.6 Hz, CH_2), 2.61 (3 H, s, Me), and 4.25 (4 H, t, NCH_2); *m*/*z* 183 (M^+, 100%).

Further elution gave **(1l)** (1.45 g, 75%) as red crystals from methanol, m.p. 165—166 °C (Found: C, 49.95; H, 6.35; N, 44.00. $C_8H_{12}N_6$ requires C, 49.99; H, 6.29; N, 43.72%); δ 2.42 (4 H, quin, *J* 7.5 Hz, CH_2) and 4.12 (8 H, t, NCH_2): *m*/*z* 192 (M^+, 100%).

3,6-*Di*(*pyrrolidin*-1-*yl*)-1,2,4,5-*tetrazine* **(1m)**.—Compound **(1f)** (1.74 g, 10 mmol) and pyrrolidine (4.43 g, 60 mmol) in a sealed glass tube were heated for 2 d at 110 °C and then worked up as described above affording **(1m)** (1.39 g, 63%) as red-brown crystals from cyclohexane, m.p. 178—179 °C (Found: C, 54.60; H, 7.40; N, 38.20. $C_{10}H_{16}N_6$ requires C, 54.52; H, 7.32; N, 38.15%); δ 1.98 (8 H, m, CH_2) and 3.52 (8 H, m, NCH_2); *m*/*z* 220 (M^+, 100%).

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