Electron Spin Resonance Study of $\mathrm{CH_3\overline{CNSSN}^{\bullet}}$, $\mathrm{C_6H_5\overline{CNSSN}^{\bullet}}$, and $\mathrm{\overline{SNSSN}^{\bullet +}}$ Free Radicals

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Isotropic and powder e.s.r. spectra have been recorded for $\mathrm{CH_3\overline{CNSSN}^{\bullet}}$, $\mathrm{C_6H_5\overline{CNSSN}^{\bullet}}$, and $\mathrm{\overline{SNSSN}^{\bullet +}}$. Isotropic labelling with nitrogen-15 and sulphur-33 has been accomplished for $\mathrm{\overline{SNSSN}^{\bullet +}}$ and it has been possible to prepare $\mathrm{\overline{^{33}S^{15}N^{33}S^{33}S^{15}N}^{\bullet +}}$. Sulphur-33 satellites have been observed for $\mathrm{C_6H_5\overline{CNSSN}^{\bullet}}$. MNDO and Gaussian 76 calculations have been used to calculate the minimum-energy structures of the radicals, while INDO calculations have provided values for the hyperfine coupling constants. Unfortunately, poor agreement was obtained between the latter and the corresponding experimental values. All the radicals dimerise in solution at low temperatures and we have been able to measure the energetics of dimerisation for $\mathrm{C_6H_5\overline{CNSSN}^{\bullet}}$ and $\mathrm{\overline{SNSSN}^{\bullet +}}$. The dimers exist as crystalline solids which contain readily detectable amounts of the monomeric free radical.

There is considerable interest in the structure and bonding properties of cyclic sulphur–nitrogen compounds.[1–4] We have studied in detail the e.s.r. isotropic and anisotropic spectra of three such compounds having similar electronic structures, (pseudo-isoelectronic), namely, 4-methyl-1,2,3,5-dithiadiazolyl (**1**), 4-phenyl-1,2,3,5-dithiadiazolyl (**2**), and 1,2,4,3,5-trithiadiazolylium (**3**).

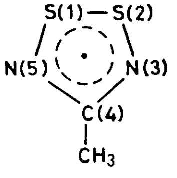
The dimer of (**1**) is a new compound and this is the first time that an e.s.r. investigation has been undertaken.

We have reported[5] briefly e.s.r. data on (**2**); here we present results from a full investigation of isotropic and anisotropic spectra.

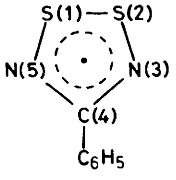
E.s.r. spectra of (**3**), prepared by a variety of methods, have been reported many times but no detailed analysis has been published, apart from our own preliminary report.[6]

Experimental

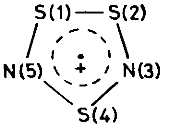
Preparation of $\mathrm{CH_3\overline{CNSSN}^{\bullet}}$ (**1**).—The dimer was prepared[7] by the electrochemical reduction of 4-methyl-1,2,3,5-dithiadiazolium chloride, $\mathrm{CH_3\overline{CNSSN}^{+}Cl^{-}}$, in a one-compartment cell;[8] the working electrode was a bright platinum strip of 2 $\mathrm{cm^2}$ area while the counter electrode was a zinc sheet of 5 $\mathrm{cm^2}$ area. The salt (0.31 g, 2 mmol) in liquid SO_2 (15 $\mathrm{cm^3}$) was electrolysed for 11 h at −15 °C with constant stirring at a constant current of 5 mA (galvano static mode). The initial potential drop across the cell of 2.2 V gradually increased to 3.1 V over a period of 10 h, while within the final hour it rose sharply to 37 V. Seconds from the start of the electrolysis the solution turned from yellow to purple and at the end of the electrolysis it was purple-black. The cell was attached to a vacuum system, the SO_2 was evaporated from the cell, and the dimer was sublimed into a trap by slowly raising the temperature to +70 °C. A yield of 85 mg of pure dimer (36%) was obtained. The dimer dissociated in toluene to give radicals.



(**1**)



(**2**)



(**3**)

At room temperature, (**1**) forms black crystals having a green metallic lustre. Although the crystals obtained by vacuum sublimation usually appear to be well developed (highly reflecting smooth facets) a number of attempts at their *X*-ray structure determination were hampered by a pronounced tendency for twinning. When an evacuated vessel containing (**1**) is cooled locally with liquid nitrogen, a deep purple deposit is formed. The vapour pressure of (**1**) as a function of temperature was measured in the range 40—95.5 °C using an all-glass sealed spring gauge: 95.5 °C is the triple point at which $p(\mathrm{MeCN_2S_2})_2 = 41.7$ Torr (Torr ≈ 133 N $\mathrm{m^{-2}}$). Within the temperature limits, the equilibrium $(\mathrm{MeCN_2S_2})_2$ (s) $\rightleftharpoons$ $(\mathrm{MeCN_2S_2})_2$ (v) closely obeys the Clausius–Clapeyron relationship (1) when p has units N $\mathrm{m^{-2}}$ or (2) when p has units Torr. Thus it seems that there is no significant dissociation into monomeric species in the vapour phase.

$$\ln p = \frac{-6\,640}{T} + 26.61 \qquad (1)$$

$$\ln p = \frac{-2\,885}{T} + 9.43 \qquad (2)$$

Preparation of $\mathrm{C_6H_5\overline{CNSSN}^{\bullet}}$ (**2**).—We have already described[5] the preparation of the dimer; the radical (**2**) is formed in high yield when the dimer is dissolved in toluene. The energetics of dimerisation have been measured in this solvent.

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Table 1. Relative isotopomer concentrations for various sulphur-33/sulphur-32 percentages[a]

	30%^{33}S/70%^{32}S	59.2%^{33}S/40.8%^{32}S	98.4%^{33}S/1.6%^{32}S
33/33/33*	2.7	20.7	95.2
33/33/32*	6.3	14.3	1.5
33/32/33*	12.6	28.6	3.0
33/32/32*	29.4	19.7	0.0
32/32/33*	14.7	9.9	0.0
32/32/32*	34.3	6.8	0.0

[a] The asterisk denotes the unique sulphur atom in $SNSSN^{\cdot +}$.

Preparation of $SNSSN^{\cdot +}$ (3).—This radical cation is formed readily when sulphur–nitrogen compounds such as S_4N_4, S_4N_2, S_7NH, and $N(SCl)_2{}^+AsF_6{}^-$ are dissolved in strong acids. Giordan *et al.*[2] have also formed the radical from a variety of sulphur–nitrogen compounds using aluminium chloride as an oxidant. Recently we have produced[9] the radical very efficiently in a novel way by adding the salts $NS_2{}^+ASF_6{}^-$ and $N(SCl)_2{}^+$-$AsF_6{}^-$ to tetrahydrofuran.

We have prepared a dimeric chloride, $S_6N_4Cl_2$ by the slow dechlorination of $S_3N_2Cl_2$ with SO_2. The product was purified by prolonged extraction with liquid SO_2 in a closed system: shiny green-black platelets (typically 5 μm wide) were formed. Gillespie *et al.*[10,11] reported that they had prepared the radical salt $SNSSN^{\cdot +}AsF_6{}^-$ but subsequently this was proved to be dimeric. Roesky and Hamza[12] have isolated a solid having the trifluoromethanesulphonate counter ion, but this is also likely to be a dimeric species; we have attempted a small scale (~ 1 mg) preparation of $SNSSN^{\cdot +}$ using their method but without success. Despite the preponderance of the dimeric species, several samples of our $(SNSSN)_2Cl_2$ gave intense e.s.r. powder spectra. We have pointed out already[6] that substitution with sulphur-33 is essential if a full evaluation of the spectral parameters of the $SNSSN^{\cdot +}$ radical is to be made: it was also shown that substitution with nitrogen-15 is important both to simplify the spectrum and to remove certain ambiguities. In our previous paper[6] we used 59.2 atom% sulphur-33 and 99.0 atom% nitrogen-15 leading to the principal isotopomer concentrations listed in Table 1. In the work reported here we have labelled the radical with two other sulphur-33 concentrations. Clearly several isotopomers can contribute to both the isotropic and the powder e.s.r. spectra. After the investigation was started, elemental sulphur containing 98.4 atom% sulphur-33 became available from Technical and Optical Equipment (London) Ltd. and this was used along with ammonia containing 99.0 atom% nitrogen to prepare $SNSSN^{\cdot +}$ radicals having a concentration of the 15/15/33/33/33* isotopomer greater than 95%. Isotopically-labelled radicals were prepared as follows. First, a milligram quantity of the labelled S_4N_4–S_4N_2 mixture was prepared by a slight modification of our published procedure;[13] 4 mg of the labelled elemental sulphur were sealed in an ampoule along with bromine (0.1 cm^3) and left overnight at room temperature. Excess bromine was pumped off and the sulphur bromide was then dissolved in dichloromethane. The solution was neutralised with a solution of 99.0 atom% nitrogen-15 labelled ammonia (Stohler Isotope Chemicals) in deuteriochloroform. The solvent was pumped off an aliquot of the solution in a 2-mm outside diameter e.s.r. sample tube, then 0.1 cm^3 of anhydrous D_2SO_4 containing 99.6 atom% deuterium (Koch-Light Ltd.) was added. The labelled $SNSSN^{\cdot +}$ radical prepared in this way was stable for several weeks when stored in liquid nitrogen.

Table 2. Isotropic hyperfine coupling constants of $CH_3CNSSN^{\cdot}$ in perdeuteriotoluene*

T/°C	a^{N-14}/mT	a^{H}/mT	a^{S-33}/mT
+8.5	0.493 ± 0.007	—	—
−8.9	0.508 ± 0.007	0.232 ± 0.003	—
−27.7	0.517 ± 0.002	0.219 ± 0.003	—
−45.2	0.511 ± 0.007	0.204 ± 0.009	—
−63.7	0.513 ± 0.005	0.200 ± 0.005	—
−80.2	0.538 ± 0.002	0.205 ± 0.002	0.645 ± 0.005
−98.7	0.528 ± 0.004	0.208 ± 0.008	0.629 ± 0.002

* The a^{S-33} values were obtained from low-field satellite lines; $g = 2.010\,44 \pm 0.000\,05$; $d(a^{N-14})/dT = -1.3 \times 10^{-3}$ mT K^{-1} and $d(a^{H})/dT = +2.7 \times 10^{-4}$ mT K^{-1}.

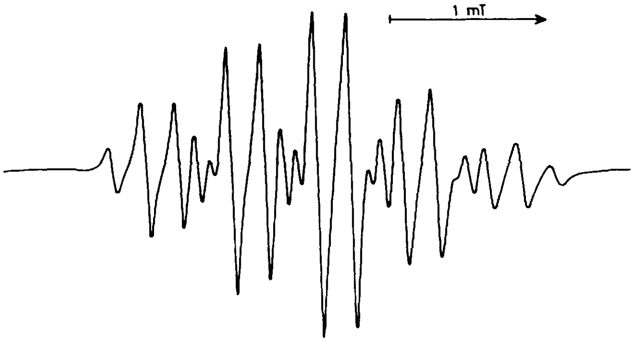


Figure 1. X-Band e.s.r. isotropic spectrum of $CH_3CNSSN^{\cdot}$ in $CFCl_3$ at −97.3 °C

Instrumentation.—The X-band e.s.r. spectra were obtained with a Varian E-4 spectrometer: spectra were calibrated using a Bruker ER 035M-1000 gaussmeter. Some spectra were digitised using a Data Dynamics 1183 paper tape punch: a computer program enabled spectra to be converted to second derivatives and line positions measured automatically. Sample temperatures were maintained to ±0.5 °C using a Varian V-4540 temperature controller. Temperatures were measured to a precision of ±0.1 °C before and after recording spectra with the aid of a Comark type 5215 digital thermometer. The g factors were measured using microcrystalline diphenylpicrylhydrazyl (dpph) as a standard.

Radical concentrations were determined by comparing the area of a spectrum with that of a known radical concentration: areas were measured with the aid of a Nicolet 1074 minicomputer. It was necessary to correct the areas for the large variation of the cavity Q with temperature for a particular solvent. This was achieved by measuring the area of the signal from solid dpph attached to the outside of a sample tube containing the solvent under investigation.

Results and Discussion

(*a*) $CH_3CNSSN^{\cdot}$ (1).—(*i*) *Isotropic spectra.* A typical X-band spectrum is shown in Figure 1 where the 1:2:3:2:1 quintet (from two equivalent nitrogen-14 nuclei) of 1:3:3:1 quartets (from the methyl group) can be seen. Coupling constants were obtained over a wide temperature range from the radical in perdeuteriotoluene solution and are presented in Table 2. From the temperature dependence of a^N and a^H one can conclude that their signs are opposite. Radical concentrations in trichlorofluoromethane, isopentane, or perdeuteriotoluene decreased at lower temperatures, but precise quantitative data could not be

Table 3. g and hyperfine interaction tensors (mT) of $CH_3\overline{CNSSN}^{\bullet}$ in perdeuteriotoluene

	g	^{14}N	H
xx	2.0026	1.43	0.242
yy	2.0090	0.08	0.242
zz	2.0215	0.11	0.242
Average	2.0110	0.541	0.242
Isotropic at −100 °C	2.0104	0.528	0.208

Table 4. Isotropic hyperfine coupling constants of $C_6H_5\overline{CNSSN}^{\bullet}$ in perdeuteriotoluene *

T/°C	$a^{N\text{-}14}$/mT	$a^{S\text{-}33}$/mT
−26.9	0.516 ± 0.002	—
−43.8	0.518 + 0.002	0.618 ± 0.004
−60.8	0.517 ± 0.005	0.616 ± 0.003
−69.7	0.516 ± 0.008	0.616 ± 0.003
−78.2	0.517 ± 0.005	0.617 ± 0.003
−87.7	0.515 ± 0.008	0.614 ± 0.003
−96.6	0.519 ± 0.003	0.612 ± 0.005
−105.5	0.524 ± 0.001	0.615 ± 0.005

* The $a^{S\text{-}33}$ values were obtained from low-field satellite lines; $g = 2.010\,19 \pm 0.000\,08$; $d(a^{N\text{-}14})/dT = -3 \times 10^{-3}$ mT K^{-1}.

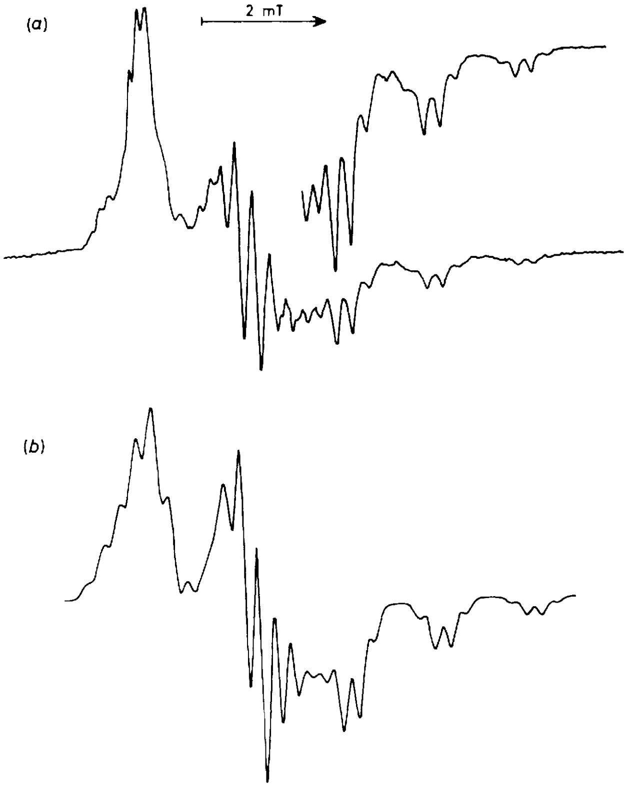


Figure 2. X-Band e.s.r. powder spectrum of $CH_3\overline{CNSSN}^{\bullet}$ in perdeuteriotoluene at −161 °C: (a) experimental and (b) computed using the parameters given in Table 3 and a linewidth of 0.25 mT

obtained for the estimation of the thermodynamic parameters of dimerisation.

(ii) *Powder spectra.* A solid sample of the 4-methyl-1,2,3,5-dithiadiazole dimer gave an intense X-band powder spectrum.

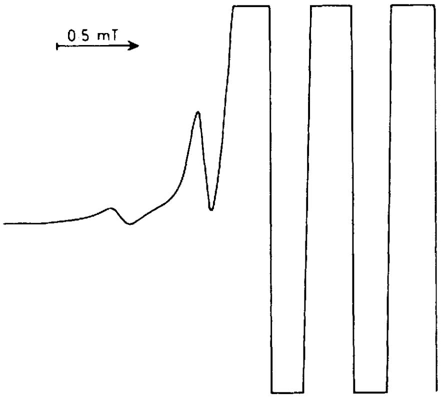


Figure 3. The low-field half of the X-band e.s.r. isotropic spectrum of $C_6H_5\overline{CNSSN}^{\bullet}$ in perdeuteriotoluene at −86.7 °C. The two weaker lines arise from the sulphur-33 satellites of the lowest field nitrogen-14 line

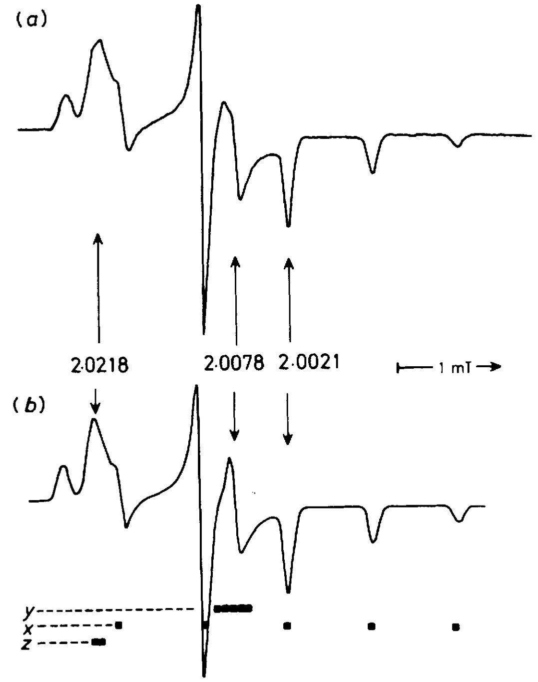


Figure 4. X-Band e.s.r. powder spectrum of $C_6H_5\overline{CNSSN}^{\bullet}$ in perdeuteriotoluene at −164 °C: (a) experimental and (b) computed using the parameters given in Table 5 and a linewidth of 0.25 mT

However, much better resolution was obtained when a frozen solution of the radical in perdeuteriotoluene was examined (see Figure 2).

The high-field section shows the well separated 1:3:3:1 quartets of the methyl group indicating that free rotation is occurring at −161 °C; these quartets are still resolved at liquid nitrogen temperature. Also depicted in Figure 2 is the best computer simulation we have been able to achieve. The spectral parameters used for the simulation are listed in Table 3 (a linewidth of 0.25 mT was used).

(b) $C_6H_5\overline{CNSSN}^{\bullet}$ (**2**).—(i) *Isotropic spectra.* The e.s.r. spectrum of the radical in perdeuteriotoluene is a simple 1:2:3:2:1 quintet from two equivalent nitrogen-14 nuclei. The simplicity of the spectrum allows the low-field sulphur-33 satellite lines to be resolved easily at temperatures below *ca.* −40 °C (see Figure 3); a hyperfine coupling constant of 0.616 ± 0.002 mT was measured which was found to be unaffected by temperature over the range −44 to −110 °C.

The low-field line from nitrogen-14 is the sharpest in the spectrum and examination of this line under the most favourable conditions gave some indication of further splitting from the protons of the phenyl group. Computer simulation (using a linewidth of 0.04 mT) suggests that there are three isotropic proton coupling constants of *ca.* 0.03 mT, the remaining two being *ca.* 0.01 mT. The isotropic parameters are listed in Table 4.

(*ii*) *Powder spectra.* As was found for the 4-methyl-1,2,3,5-dithiadiazole dimer, the solid 4-phenyl dimer gave an intense ill resolved powder spectrum. Again the frozen perdeuteriotoluene solution gave a well resolved e.s.r. spectrum. The experimental and computer-simulated spectra are depicted in Figure 4: the data used for the simulation are given in Table 5.

(*iii*) *Energetics of dimerisation of* $C_6H_5\overline{CNSSN}^{\bullet}$. The change of radical concentration with temperature was measured (see Table 6). It was found that almost no dimer is present above *ca.* 250 K, hence the temperature of 200 K was chosen for the evaluation of ΔG and ΔS for the dimerisation process. The dimerisation constant, K, was calculated from the expression (3), where R is the radical concentration at a given temperature

$$K = (R_0 - R)/2R^2 \qquad (3)$$

and R_0 is the radical concentration at the higher temperatures where no dimers are present; the value of R_0 was found by extrapolation. From the dependence of K on temperature we evaluated ΔH, ΔG_{200}, and ΔS_{200} for the dimerisation process (see Table 6).

Table 5. g and hyperfine interaction tensors (mT) of $C_6H_5\overline{CNSSN}^{\bullet}$ in perdeuteriotoluene

	g	^{14}N
xx	2.0021	1.410
yy	2.0078	0.107
zz	2.0218	0.035
Average	2.0106	0.517
Isotropic at −97 °C	2.0102	0.519

Table 6. Dimerisation of $C_6H_5\overline{CNSSN}^{\bullet}$ in toluene and of $\overline{SNSSN}^{\bullet +}Cl^-$ in $SOCl_2$–SO_2 (4:1 v/v)

$C_6H_5\overline{CNSSN}^{\bullet}$ [a]		$\overline{SNSSN}^{\bullet +}Cl^-$ [b]	
T/K	Radical concentration/mol dm^{-3}	T/K	Radical concentration/mol dm^{-3}
263	1.23×10^{-3}	281	2.11×10^{-6}
246	1.19	272	1.56
230	1.09	262	9.9×10^{-7}
213	8.9×10^{-4}	253	6.4
204	7.4	244	3.6
195	5.2	235	2.1
190	4.2	226	1.5
186	3.1	217	9.6×10^{-8}
181	2.6	208	6.7
177	1.5	199	3.7

[a] $\Delta H = -35(\pm 2)$ kJ mol^{-1}, $\Delta G_{200} = -12(\pm 1)$ kJ mol^{-1}, and $\Delta S_{200} = -120(\pm 10)$ J K^{-1} mol^{-1}. [b] $\Delta H = -47(\pm 7)$ kJ mol^{-1}.

The negative value of ΔS_{200} is to be expected since more order is introduced into the system by dimerisation. We have obtained similar values of ΔS for the dimerisation of the nitrogen-centred dithiazolidinyl radicals.[14] The value of ΔH is similar to those reported in the literature[15–17] for the dimerisation of a variety of radicals. It should be pointed out that previous workers did not appear to have made the all-important corrections[18] for variation of the e.s.r. cavity quality factor, Q, with temperature.

(*c*) $\overline{SNSSN}^{\bullet +}$ (3).—(*i*) *Isotropic spectra.* A particularly intense e.s.r. spectrum of this radical is observed when $NS_2{}^+$-$AsF_6{}^-$ is dissolved in tetrahydrofuran.[9] From such a spectrum we found a^{N-14} to be 0.319 ± 0.001 mT and low-field satellites of sulphur-33 gave a value for $a^{S-33(2)}$ of 0.872 ± 0.007 mT; unlike the radicals $CH_3\overline{CNSSN}^{\bullet}$ and $C_6H_5\overline{CNSSN}^{\bullet}$, there is no discernible dependence of these values on temperature in the range +22 to −44 °C, and similar values were found when acetonitrile was the solvent. Lipp *et al.*[19] found similar coupling constants for the radical generated from S_4N_4 and H_2SO_4. They also prepared S_4N_4 enriched with 48.6 atom% of sulphur-33, and from the resulting spectrum presumed that only two equivalent sulphurs were present and that the radical was $S_2N_2{}^{\bullet +}$. This misassignment was made because the unique sulphur in $\overline{SNSSN}^{\bullet +}$ has a hyperfine coupling constant almost identical with that for ^{14}N. We overcame this difficulty by labelling the radical with 99.0 atom% nitrogen-15 which allowed the coupling constant for the unique sulphur to be measured.[6] We also labelled the radical with 98.4 atom% sulphur-33. This led to the finding of another curiosity, namely that the coupling constant for the equivalent sulphurs is almost exactly twice that of ^{14}N. These findings are summarised in Table 7 and the isotropic spectrum of the fully-labelled radical, $\overline{^{33}S^{15}N^{33}S^{33}S^{15}N}^{\bullet +}$ is depicted in Figure 5. The severe broadening apparent in the wings of the spectrum is due to incomplete averaging of the considerable anisotropy in the nitrogen-15 and the sulphur-33 hyperfine interaction tensors. Precise values of the isotropic coupling constants were obtained in the following way, (i) a^{N-14} from the unlabelled radical, (ii) $a^{S-33(2)}$ from the sulphur-33 satellites of the unlabelled and nitrogen-15 labelled radical, (iii) a^{N-15} from the nitrogen-15 labelled radical, (iv) $a^{S-33(1)}$ from the radical labelled with sulphur-33 and nitrogen-15. It should be noted that $a^{S-33(1)}$

Table 7. g and hyperfine interaction tensors (mT) for $\overline{SNSSN}^{\bullet +}$ in D_2SO_4

	g	^{14}N	^{15}N	$^{33}S(2)$	$^{33}S(1)$
xx	2.0013	0.918	1.285	3.784	0.893
yy	2.0062	~0	~0	~0	~0
zz	2.0250	~0	~0	(−)0.882	~0
Average	2.0108	0.306	0.428	0.967	0.298
Isotropic[a,b]	2.011 12 ± 0.000 01	0.319 ± 0.001	0.446 ± 0.003[c]	0.861 ± 0.007[d]	0.297 ± 0.004

[a] At +22.0 °C. [b] From $NS_2{}^+AsF_6{}^-$ in tetrahydrofuran at +17.6 °C: $g = 2.010\,85 \pm 0.000\,09$, $a^{N-14} = 0.319 \pm 0.001$ mT, and $a^{S-33(2)} = 0.872 \pm 0.007$ mT. [c] From $\overline{S^{15}NSS^{15}N}^{\bullet +}$. [d] From ^{33}S satellites of $\overline{SNSSN}^{\bullet +}$ and $\overline{S^{15}NSS^{15}N}^{\bullet +}$.

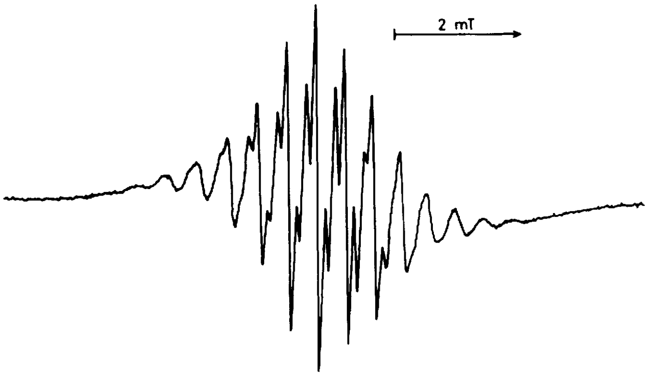


Figure 5. X-Band e.s.r. isotropic spectrum of $\overline{^{33}\mathrm{S}^{15}\mathrm{N}^{33}\mathrm{S}^{33}\mathrm{S}^{15}\mathrm{N}}^{\cdot+}$ in anhydrous D_2SO_4 at +22 °C

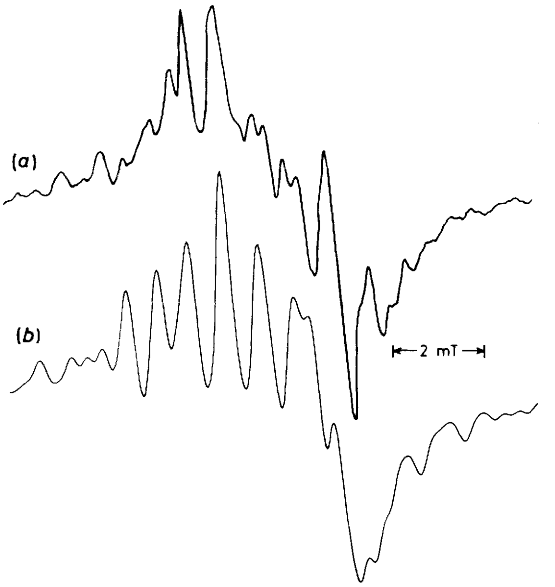


Figure 6. X-Band e.s.r. powder spectrum of $\overline{^{33}\mathrm{S}^{15}\mathrm{N}^{33}\mathrm{S}^{33}\mathrm{S}^{15}\mathrm{N}}^{\cdot+}$ in D_2SO_4 at −141.6 °C: (*a*) experimental and (*b*) computed using the parameters given in Table 7

cannot be measured from the low-field satellites of the spectrum of the unenriched radical because of another coincidence, namely that $\frac{1}{2}a^{\text{S-33(2)}} \sim \frac{3}{2}a^{\text{S-33(1)}}$.

(*ii*) *Powder spectra.* As for the dimers of (**1**) and (**2**), the dimer of (**3**), namely the purple solid $(\overline{\mathrm{SNSSN}})_2\mathrm{Cl}_2$, gives an intense poorly resolved e.s.r. spectrum showing that (**3**) is present in an appreciable amount. A well resolved and simplified spectrum can be obtained by examining a frozen solution of $\overline{\mathrm{S}^{15}\mathrm{NSS}^{15}\mathrm{N}}^{\cdot+}$ in D_2SO_4 (see ref. 6). It is obvious from this spectrum that most of the spin density is localised in nitrogen p orbitals lying at right angles to the ring (the x direction), as found for radicals (**1**) and (**2**).

Because we were able to label radical (**3**) with sulphur-33, we had the possibility of determining the sulphur p orbital contributions [unfortunately, labelling radicals (**1**) and (**2**) with sulphur-33 is not a practical proposition]. Two sets of labelling experiments were performed, one with 98.4 atom% and one with 30 atom% sulphur-33, the nitrogen-15 content being 99 atom% in both cases. The 98.4% ^{33}S spectrum (Figure 6) was disappointingly uninformative. It did, however, show that (i) little or no ^{33}S hyperfine coupling is associated with g_{yy} (2.0062), (ii) large hyperfine couplings exist between the unpaired electron and two equivalent ^{33}S nuclei when $B_0//x$, and (iii) couplings of 0.88 mT with two equivalent sulphur nuclei are seen when $B_0//z$. A spectrum from a 30% ^{33}S sample was examined (Figure 7) in order to minimize interference from doubly-labelled free radicals and to simplify the powder spectrum. The wide manifold of 1:2:1 ^{15}N triplets for $B_0//x$ was clearly observed in the wings of the spectrum and permitted a precise determination of a_{xx} for the two equivalent ^{33}S nuclei (Table 7). For that canonical direction a further coupling of 0.89 mT to a unique ^{33}S was evident. Broadening of the wide (xx) sulphur manifold was severe and very apparent in the high-field portion of the 30% ^{33}S spectrum. We were unable to simulate such extreme broadening with our computer program, and believe it may be due to residual internal motion of the radical. A good simulation of the 30% ^{33}S spectrum was generated (Figure 7) with the data of Table 7, but we were unable to obtain a good match to the 98.4% spectrum because of the distortions from asymmetric line broadening. Further experiments at 4 K using a Q-band spectrometer are planned to resolve this problem.

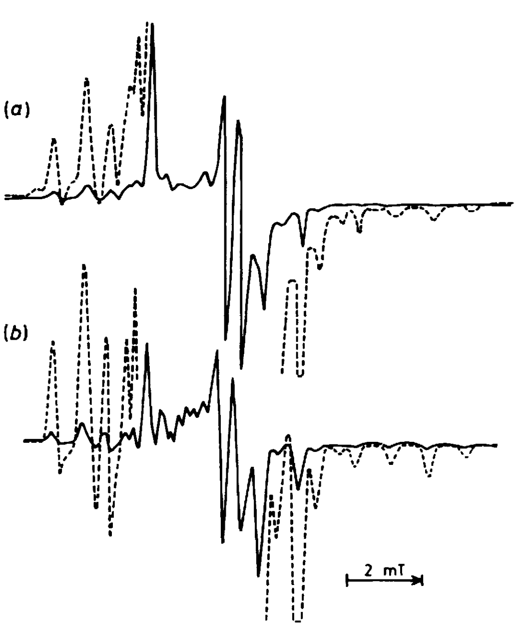


Figure 7. X-Band e.s.r. powder spectrum of $\overline{\mathrm{S}^{15}\mathrm{NSS}^{15}\mathrm{N}}^{\cdot+}$, labelled with 30 atom% sulphur-33, in D_2SO_4 at −160 °C: (*a*) experimental and (*b*) computed using the parameters given in Table 7. The broken lines represent spectra run at high gain

The anisotropic hyperfine parameters deduced for $\overline{\mathrm{SNSSN}}^{\cdot+}$ differ from our earlier estimates[6] and lead to a much improved unpaired-spin count. Using the data of Table 7 and appropriate one-electron parameters, we estimate the following valence atomic orbital spin populations for $\overline{\mathrm{SNSSN}}^{\cdot+}$: 2N (0.5% 2$s$, 25.0% 2$p_x$); 2S (0.7% 3$s$, 36.8% 3$p_x$, 6.7% 3$p_z$); 1S (0.2% 3$s$, 8.5% 3$p_x$). Assuming positive spin densities for the equivalent pairs of nuclei and negative values for the unique sulphur,[6] the total unpaired spin population is 111%, a most satisfying result.

(*iii*) *Energetics of dimerisation of* $\overline{\mathrm{SNSSN}}^{\cdot+}$. For these experiments we employed a saturated solution of $(\overline{\mathrm{SNSSN}})_2\mathrm{Cl}_2$ in $SOCl_2$–SO_2 (4:1 v/v). The effect of temperature on the e.s.r. cavity Q was measured for this solvent mixture. The cavity Q correction was made when determining the concentrations of

Table 8. Minimum-energy structures for $CH_3CNSSN^{\cdot}$

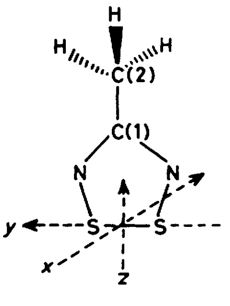
	Average *X*-ray data[20] for $C_6H_5CNSSN^{\cdot}$	Gaussian 76	MNDO
S–S/Å	2.089	2.099	2.069
S–N/Å	1.625	1.717	1.605
N–C/Å	1.334	1.372	1.364
C–C/Å	1.473	1.530	1.516
SSN/°	94.1	94.8	94.0
SNC/°	115.1	114.6	113.6
NCN/°	121.1	121.2	119.0
α/°	0	181.0	179.3
Binding energy* from INDO	−2.521	−3.100	−3.062

* Atomic units.

$SNSSN^{\cdot +}$ given in Table 6. Since we have not been able to measure the total concentration of $(SNSSN)_2^{2+}$ plus $SNSSN^{\cdot +}$ at any temperature, it is not possible to obtain a value of ΔG (and hence ΔS) for the dimerisation process. From Table 6 it may be seen that the value of ΔH we determined is similar to that found for the dimerisation of $C_6H_5CNSSN^{\cdot}$ (**2**). However, the value of ΔS could be very different since we are dealing with ionic species in a polar medium.

Calculations of Minimum-energy Structures and Hyperfine Coupling Constants.—Although *X*-ray data are available for crystals of the dimer of $C_6H_5CNSSN^{\cdot}$[20] and for salts of $SNSSN^{\cdot +}$,[7] calculated structures of the isolated radicals are most likely to reflect the properties of the radicals in solution. Minimum-energy structures of the radicals were calculated using either the Gaussian 76 geometry optimisation program[21] on the University of Manchester CDC 7600 computer, or from the MNDO program[22] on the University of Liverpool VAX 11/780 computer. The minimum-energy structures thus calculated were then used to obtain binding energies and hyperfine coupling constants using a modified[23] INDO program[24] on the University of Liverpool IBM 3083 computer. Gaussian 76 calculations are generally regarded as being superior to those of MNDO; however, Gaussian 76 calculations either did not converge or find a minimum for $SNSSN^{\cdot +}$. Isotropic (*a*) and anisotropic (*A*) components of the hyperfine interaction tensors were obtained from the computed *s* and *p* spin densities, respectively, using the appropriate one-electron parameters.[25]

(*i*) $CH_3CNSSN^{\cdot}$ (**1**). The axes chosen for this radical are shown below. MNDO and Gaussian 76 geometry-optimised structures were obtained using trial dimensions from the *X*-ray data found for the dimer of $C_6H_5CNSSN^{\cdot}$. In order to save time and expense only the heterocyclic ring dimensions were optimised and the methyl group bond lengths and angles were kept constant at 1.09 Å and 109° respectively.



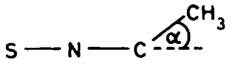


Table 8 lists the *X*-ray geometry and the optimised geometries along with the binding energies calculated with INDO. A significant improvement in the minimum binding energies resulted from the calculations. The latter predicted that the methyl group is slightly out of plane. The Gaussian 76 structure and the *X*-ray derived data were used to calculate the hyperfine coupling constants given in Table 9. While the two sets of computer coupling constants are in agreement with one another, there is generally poor agreement with the experimental values. This contrasts with the results we obtained previously[26] for some other cyclic nitrogen–sulphur containing radicals.

(*ii*) $C_6H_5CNSSN^{\cdot}$ (**2**). The co-ordinate system used is shown below. *X*-Ray data are available for the dimer of the radical and these were used to calculate both the MNDO and the Gaussian 76 optimised structures (see Table 10). In order to save computer time, the bond parameters of the phenyl ring were

Table 9. Calculated and experimental hyperfine coupling constants of $CH_3CNSSN^{\cdot}$

Coupling constant[a]	Calculated		
	X-Ray[b]/mT	Gaussian 76/mT	Experimental/mT
a^S	0.12	0.11	0.64
A_x^S	1.03	0.82	—
A_y^S	−0.43	−0.29	—
A_z^S	−0.60	−0.53	—
a^N	1.51	1.57	0.528
A_x^N	2.06	2.26	0.89
A_y^N	−1.04	−1.15	−0.46
A_z^N	−1.02	−1.11	−0.43
$a^{C(1)}$	−2.67	−3.21	—
$A_x^{C(1)}$	−2.19	−2.50	—
$A_y^{C(1)}$	1.05	1.20	—
$A_z^{C(1)}$	1.14	1.30	—
$a^{C(2)}$	0.58	0.69	—
$A_x^{C(2)}$	0.07	0.07	—
$A_y^{C(2)}$	−0.06	−0.07	—
$A_z^{C(2)}$	−0.01	0.00	—
a^H	−0.85	−0.95	0.208

[a] *a* is the isotropic, *A* the anisotropic coupling; the net coupling along *x* for example is $a_x = a + A_x$. [b] *X*-Ray data for $C_6H_5CNSSN^{\cdot}$ were used.

Table 10. Minimum-energy structures and *X*-ray data for $C_6H_5CNSSN^{\cdot}$

	Average *X*-ray data[20]	Optimised from β = 0°		Optimised from β = 45°	
		Gaussian 76	MNDO	Gaussian 76	MNDO
S–S/Å	2.095	2.116	2.023	2.116	2.023
S–N/Å	1.60	1.642	1.595	1.642	1.595
N–C/Å	1.370	1.378	1.356	1.378	1.356
$C–C_6H_5$/Å	1.450	1.494	1.481	1.494	1.481
SSN/°	94.9	95.1	95.5	94.5	95.5
SNC/°	115.0	115.3	115.4	115.3	115.4
NCN/°	120.5	120.0	119.4	120.0	119.4
α/°	0.0	0.0	0.2	0.0	0.2
β/°	0.0	0.1	0.6	17.8	55.1
Binding energy* from INDO	−7.854	−7.857	−7.852	−7.857	−7.843

* Atomic units.

Table 11. Calculated and experimental hyperfine coupling constants of $\mathrm{C_6H_5\overline{CNSSN}^{\bullet}}$

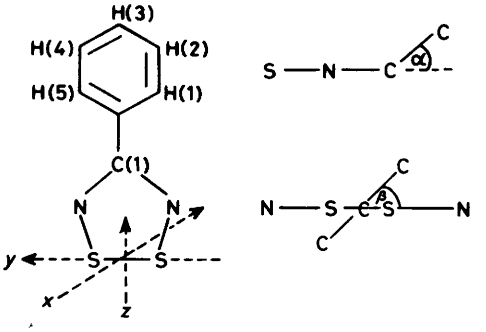
Coupling constant[*]	Calculated X-Ray/mT	Calculated Gaussian 76/mT	Experimental/mT
a^{S}	0.12	1.11	0.615
A_x^{S}	1.03	0.96	—
A_y^{S}	−0.43	−0.38	—
A_z^{S}	−0.60	−0.58	—
a^{N}	1.59	1.62	0.519
A_x^{N}	2.09	2.22	0.893
A_y^{N}	−1.06	−1.12	−0.410
A_z^{N}	−1.03	−1.10	−0.483
$a^{C(1)}$	−3.11	−3.26	—
$A_x^{C(1)}$	−2.12	−2.46	—
$A_y^{C(1)}$	1.01	1.18	—
$A_z^{C(1)}$	1.11	1.28	—
$a^{H(1)}$	0.19	0.17	~0.03
$a^{H(2)}$	−0.11	−0.09	~0.01
$a^{H(3)}$	0.16	0.14	~0.03

[*] a is the isotropic, A the anisotropic coupling; the net coupling along x for example is $a_x = a + A_x$.

Table 12. Minimum-energy structures and X-ray data for $\overline{\mathrm{SNSSN}}^{\bullet +}$

	X-Ray[7]	MNDO
S–S/Å	2.147	2.118
S(1)–N/Å	1.606	1.561
N–S(4)/Å	1.560	1.578
S(1)S(2)N/°	96.6	91.6
S(1)NS(4)/°	119.9	121.9
NS(4)N/°	107.2	101.2
α/°	0	0
Binding energy[*] from INDO	−0.375	−0.359

[*] Atomic units.

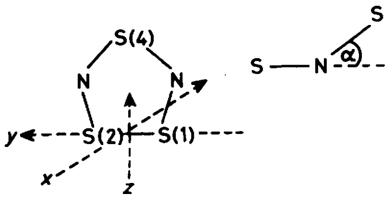


kept constant with C–C = 1.38 Å, C–H = 1.09 Å and CCC and CCH bond angles of 120°. Both types of calculation had to be performed with a multiplicity of 1 rather than 2, otherwise the MNDO and Gaussian 76 programs failed to converge. The results predict that the heterocyclic ring is planar and from Table 10 it may be seen that α is essentially zero. The angle of twist (β) is apparently not zero but the Gaussian 76 minimum energies optimised from β = 0 and β = 45° are essentially equal (see Table 10). Hyperfine coupling constants were calculated from the Gaussian 76 and the X-ray structural parameters; the agreement with the experimental coupling constants is poor (see Table 11).

Table 13. Calculated and experimental hyperfine coupling constants of $\overline{\mathrm{SNSSN}}^{\bullet +}$

Coupling constant[*]	Calculated X-Ray/mT	Calculated MNDO/mT	Experimental/mT
$a^{S(1)}$	0.22	0.25	0.872
$A_x^{S(1)}$	1.50	1.65	2.817
$A_y^{S(1)}$	−0.67	−0.76	−0.967
$A_z^{S(1)}$	−0.83	−0.89	−1.849
a^{N}	1.38	1.35	0.319
A_x^{N}	1.78	1.69	0.612
A_y^{N}	−0.90	−0.86	−0.306
A_z^{N}	−0.88	−0.83	−0.306
$a^{S(4)}$	−0.07	−0.09	0.297
$A_x^{S(4)}$	−2.09	−2.05	0.595
$A_y^{S(4)}$	1.04	1.01	—0.298
$A_z^{S(4)}$	1.05	1.04	—0.298

[*] a is the isotropic, A the anisotropic coupling; the net coupling along x for example is $a_x = a + A_x$.



(*iii*) $\overline{\mathrm{SNSSN}}^{\bullet +}$ (3). The axes used for this radical are shown below. Gaussian 76 calculations were not able to provide a minimum-energy structure even when *d* orbitals were included: such an inclusion has been recommended[27] when two second-row elements are adjacent to one another in a molecule. MNDO calculations were successful (see Table 12) and showed the molecule to be planar, in agreement with the X-ray data.[7] The calculations also show that the dimensions of the isolated molecule are considerably different from those of the crystal, possibly because ions are involved. In Table 13 are listed the hyperfine coupling constants found experimentally and by calculation. Again, there is poor agreement between the two sets of data. However, it is interesting that the rather different molecular dimensions found from X-ray measurements and MNDO calculations still generate very similar hyperfine interactions.

Conclusions

The MNDO calculations indicate that the molecular geometries of the heterocyclic rings of $\mathrm{CH_3\overline{CNSSN}^{\bullet}}$ (1) and $\mathrm{C_6H_5\overline{CNSSN}^{\bullet}}$ (2) are very similar (see Tables 8 and 10), whereas $\overline{\mathrm{SNSSN}}^{\bullet +}$ (3) has a longer S–S bond and a shorter S(1)–N bond (see Table 12). The effect of these structural differences appears to place a larger spin density on the S(1) and S(2) atoms of the latter radical, and a smaller spin density on the nitrogen atoms. X-Ray crystallography has shown that the dimer of (2) has the heterocyclic rings in a *cis* configuration[20] while the rings in $(\overline{\mathrm{SNSSN}})_2\mathrm{Cl_2}$ are *trans*:[7] the rings in both compounds are held together with two long (2.916 Å) sulphur–sulphur bonds.

Despite the structural differences, the dimers of (1), (2), and (3) appear reversibly to dissociate readily even to the extent that appreciable amounts of radical are present in the dimeric solids. It is this fact which probably misled Gillespie *et al.*[10] into believing that they had isolated crystals of $\overline{\mathrm{SNSSN}}^{\bullet +}\mathrm{AsF_6}^{-}$.

Acknowledgements

The authors are indebted to Mr. J. Brunskill for his advice on the molecular-orbital calculations. A. J. B. and Z. V. H. thank the S.E.R.C. for a research grant.

References

1 H. W. Roesky, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 91.

2 J. Giordan, H. Bock, M. Eiser, and H. W. Roesky, *Phosphorus Sulphur*, 1982, **13**, 19.

3 A. H. Cowley, S. K. Mehrotra, and H. W. Roesky, *Inorg. Chem.*, 1983, **22**, 2095.

4 T. Chivers, *Acc. Chem. Res.*, 1984, **17**, 166.

5 A. J. Banister, N. R. M. Smith, and R. G. Hey, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1181.

6 S. A. Fairhurst, K. F. Preston, and L. H. Sutcliffe, *Can. J. Chem.*, 1984, **63**, 1124.

7 R. W. Small, A. J. Banister, and Z. V. Hauptman, *J. Chem. Soc., Dalton Trans.*, 1984, 1377.

8 A. J. Banister, Z. V. Hauptman, and A. G. Kendrick, *J. Chem. Soc., Chem. Commun.*, 1983, 1016.

9 S. A. Fairhurst, A. Hulme-Lowe, K. M. Johnson, L. H. Sutcliffe, J. Passmore, and M. J. Schriver, *Magn. Reson. Chem.*, 1985, **23**, 828.

10 R. J. Gillespie, P. R. Ireland, and J. E. Vekris, *Can. J. Chem.*, 1975, **53**, 3147.

11 R. J. Gillespie, J. P. Kent, and J. F. Sawyer, *Inorg. Chem.*, 1981, **20**, 3784.

12 H. W. Roesky and A. Hamza, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 226.

13 S. Apter, M. Carruthers, and L. H. Sutcliffe, *Inorg. Chim. Acta*, 1978, **31**, L445.

14 N. J. Stewart and L. H. Sutcliffe, unpublished work.

15 A. G. Evans, J. C. Evans, and M. W. Baker, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1787.

16 S. Tero-Kubota, Y. Sano, and Y. Ikegami, *J. Am. Chem. Soc.*, 1982, **104**, 3711.

17 K. Schlosser and S. Steenken, *J. Am. Chem. Soc.*, 1983, **105**, 1504.

18 D. P. Dalal, S. S. Eaton, and G. R. Eaton, *J. Magn. Reson.*, 1981, **44**, 415.

19 S. A. Lipp, J. J. Chang, and W. L. Jolly, *Inorg. Chem.*, 1970, **9**, 1070.

20 A. Vegas, A. Pérez-Salazar, A. J. Banister, and R. G. Hey, *J. Chem. Soc., Dalton Trans.*, 1980, 1812.

21 J. S. Binkley, R. A. Whiteside, P. C. Hanharan, R. Seeger, J. A. Pople, W. J. Hehre, and H. N. Newton, Program No. 368, Quantum Chemistry Program Exchange, Bloomington, Indiana, 1976.

22 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899.

23 M. D. Beer and R. Grinter, *J. Magn. Reson.*, 1977, **26**, 421.

24 J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 1967, **47**, 2026; Program No. 141, Quantum Chemistry Program Exchange, Bloomington, Indiana, 1967.

25 J. R. Morton and K. F. Preston, *J. Magn. Reson.*, 1978, **30**, 577.

26 G. K. MacLean, J. Passmore, M. N. Sudheedra Rao, M. J. Schriver, P. S. White, D. Bethel, R. S. Pilkington, and L. H. Sutcliffe, *J. Chem. Soc., Dalton Trans.*, 1985, 1405.

27 J. B. Collins, P. von R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, 1978, **64**, 5142.

Received 7th October 1985; *Paper* 5/1726