One-electron Reduction of Di-imidosulphur Compounds, $S(NR)_2$, and some Complexes of Group 6A Metal Carbonyl Derivatives containing $S(NR)_2$ Ligands: Studies of the Radical Products by Electron Spin Resonance Spectroscopy

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Reduction of the di-imidosulphur compounds, $S(NR)_2$ ($R = Bu^t$, Ph, $4\text{-}MeC_6H_4$, or $4\text{-}O_2NC_6H_4$), in 1,2-dimethoxyethane solution with a potassium mirror *in vacuo* gives fairly stable solutions of the corresponding anion radicals $[S(NR)_2]^-$ which have been studied by e.s.r. spectroscopy. The frozen-solution e.s.r. spectrum of $K[S(NBu^t)_2]$ has also been recorded. Isotropic coupling constants $A(^{14}N)$, $A(^1H)$ and, for $R = Bu^t$, $A(^{33}S)$ have been deduced and analysed in terms of the electronic structures of the radicals using empirical electron-density relationships. Some CNDO/2 and INDO calculations have been made and the experimental and calculated electron-spin densities compared. Variable-temperature e.s.r. measurements have given no indication of the presence of distinct geometric isomers of the anions in solution. The model calculations suggest that the *E*/*E* conformation is most stable and that interconversion to give the *E*/*Z* or *Z*/*Z* forms is unlikely. The experimental evidence in all cases indicates the two nitrogen atoms to be magnetically equivalent. Alkali-metal isotropic coupling constants $A(M^I)$ for the species $M^I[S(NBu^t)_2]$ ($M^I = {}^7Li$, ${}^{23}Na$, or ${}^{39}K$) have been estimated and indicate that the metal–anion interaction increases in the order $K < Na < Li$.

Potassium-metal reduction of $[M(CO)_4\{S(NBu^t)_2\}]$ (M = Cr, Mo, or W) produces the corresponding anions with well defined isotropic e.s.r. spectra. Values for $A(^{14}N)$ and $A(M)$ ($M = {}^{95/97}Mo$ or ${}^{183}W$) have been deduced and the spectra analysed. The results suggest that the unpaired electron is located mainly in the $S(NBu^t)_2$ ligand. CNDO/2 calculations for the chromium anion are consistent with this observation. Attempts to produce $[M(CO)_4\{S(NPh)_2\}]^-$ have been unsuccessful except for M = Cr, when an unstable species is formed. A tentative analysis of the e.s.r. spectrum of this radical anion is presented.

THERE has been considerable recent interest in the properties of compounds containing sulphur–nitrogen double bonds.[1] In this context, the chemistry of substituted di-imidosulphur compounds, $S(NR)_2$, has received attention. These compounds have been shown to undergo a range of organic reactions [2] and also to form various complexes with transition metals.[3–5] Although anion radicals of 1,2,5-thiadiazole [6–8] and a few related heterocyclic compounds containing NSN systems [7–9] have been studied, no attention has been paid to the one-electron reduction products of simple di-imidosulphur derivatives.

Three possible planar structural conformations are predicted for the RNSNR system: *E*/*E*, *E*/*Z*, and *Z*/*Z*. The most stable form appears generally to be *E*/*Z*, as shown by n.m.r. measurements,[4a,10] electron diffraction,[11] and *X*-ray studies [12] of various compounds. An *E*/*E* configuration for the $S(NBu^t)_2$ fragment in a trialkyl sulphur di-imide cation has recently been reported.[13] This arrangement is also in general supported by theoretical calculations using the CNDO/2 method [14,15] although it is asserted that in the case of $S(NMe)_2$ the *E*/*E* form is slightly more stable.[15] The calculations also suggest that the barrier to interconversion amongst the various conformers is likely to be sufficiently small for a mixture of differently oriented molecules generally to be present.

The same configurations, at least, are likely to be important for the radical anions. The lowest unoccupied molecular orbital (l.u.m.o.) of the neutral molecules is a π^* orbital localised on the sulphur atom. It is thus into this orbital that the additional electron for the formation of the radical anion is expected to go. The ready formation of odd-electron species by reaction of the di-imides with alkali metals is therefore a reasonable prediction. We report here the formation of some such radical anions and of related species derived from Group 6A transition-metal complexes of $S(NR)_2$. The properties of the radicals have been examined by e.s.r. spectroscopy and attempts have been made to obtain some correlation with the results of suitable approximate molecular orbital (m.o.) calculations.

EXPERIMENTAL

The *NN'*-disubstituted di-imidosulphur compounds $S\{N(C_6H_4X\text{-}4)\}_2$ ($X = H$, Me, or NO_2),[16] $S(NBu^t)_2$,[17] and $S(NMe)_2$[4a,18] were prepared and purified, as were the complexes $[M(CO)_4\{S(NBu^t)_2\}]$ [3] (M = Cr, Mo, or W), by methods previously described. Attempts to synthesise the analogous metal complexes containing phenyl groups were made using the same procedure and, alternatively, from $[M(CO)_5(thf)]$ (thf = tetrahydrofuran) using method A of Vrieze and co-workers [4b] (see Results section).

1,2-Dimethoxyethane was purified by distillation, finally *in vacuo* from sodium diphenylketyl.

Radicals were produced *in vacuo* ($<10^{-3}$ Torr) † in 1,2-dimethoxyethane solution by reduction with alkali-metal film (Na or K) or with freshly cut metal (Li) at ambient temperature. Radical concentrations were optimised by distillation in the e.s.r. cell. Electron spin resonance spectra were recorded with a JEOL PE1 *X*-band spectrometer fitted with a variable-temperature facility. The necessary calibrations were made with diphenylpicrylhydrazyl and potassium peroxylaminedisulphonate.

RESULTS

Reduction of $S(NBu^t)_2$ with alkali metal (Li, Na, or K) in 1,2-dimethoxyethane gives deep purple solutions stable

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† Throughout this paper: 1 Torr = (101 325/760) Pa.

for several hours at ambient temperature. These solutions give rise to strong symmetrical e.s.r. signals comprising five major lines of relative intensities 1 : 2 : 3 : 2 : 1 (Figure 1).

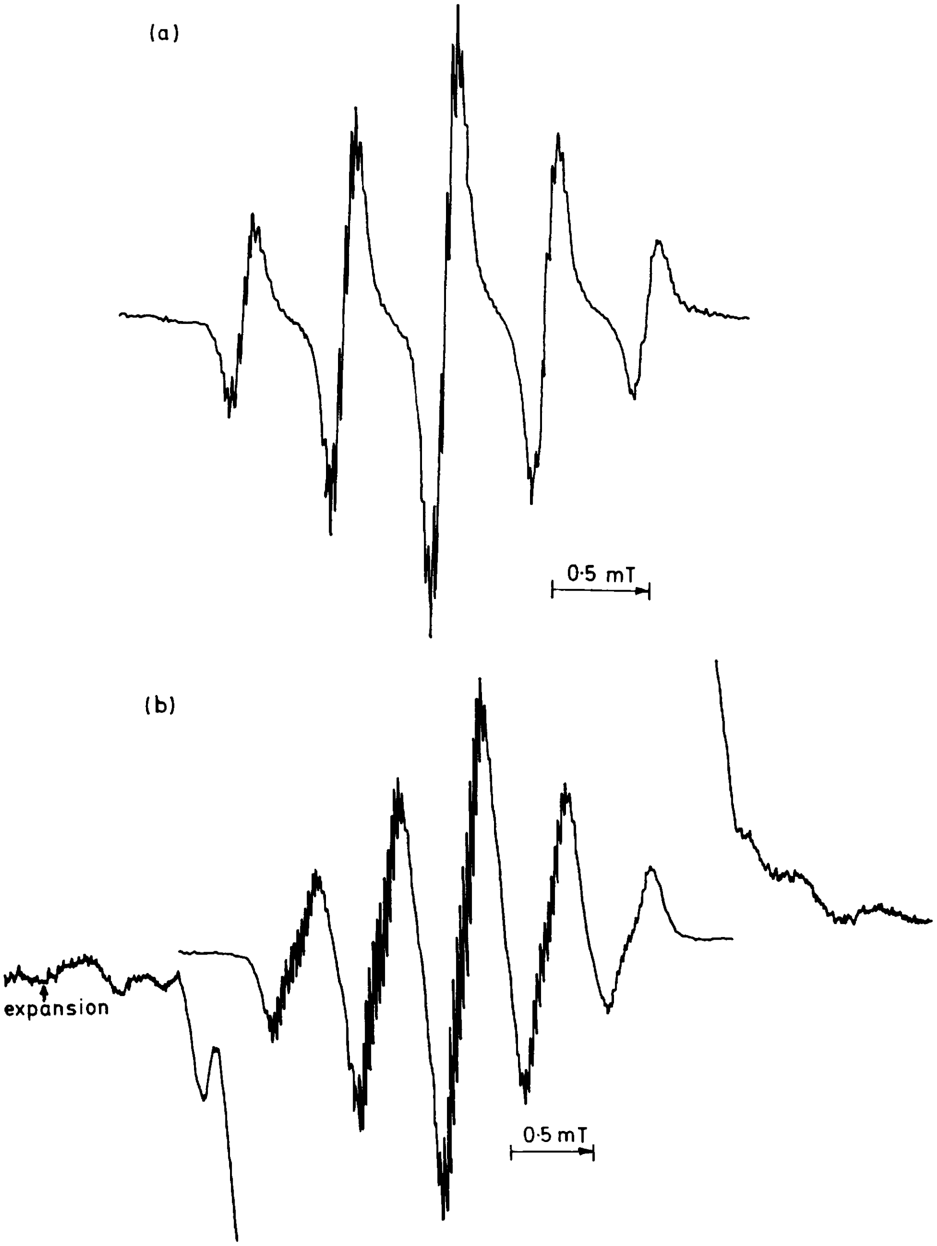


FIGURE 1 E.s.r. spectrum of $[S(NBu^t)_2]^-$ in 1,2-dimethoxyethane solution at *ca.* 10 °C: (a) K^+ gegenion, (b) Na^+ gegenion

When potassium is used as reductant, a variation in temperature over the range −50 to 20 °C causes no marked change in the signal. Smaller hyperfine splittings which are evident may be assigned to coupling with ^1H atoms in equivalent Bu^t groups. With higher spectrometer gain, satellites attributable to interaction with ^{33}S ($I = \frac{3}{2}$, 0.74%) are observed. It thus appears that a single species $[S(NBu^t)_2]^-$ is present along with K^+ gegenions.

A frozen solution of $K[S(NBu^t)_2]$ in 1,2-dimethoxyethane at *ca.* −140 °C gives an e.s.r. spectrum assignable to an axially symmetric species.

When lithium or sodium is used for the reduction, a similar five-line symmetrical spectrum is obtained, but with additional hyperfine structure compared with the product from potassium reduction (Figure 1). Line-width changes occur with variation in temperature, particularly with the sodium reduction product, with which a line-width reduction of some 25% occurs between −50 and 60 °C and the hyperfine structure is lost at the higher temperatures. The extra splittings are assigned to alkali-metal coupling.

Attempts to produce the analogous $[S(NMe)_2]^-$ radical anion by reduction of the parent di-imide with potassium film under identical conditions gave no detectable e.s.r. signals. No marked colour change was observed, but a yellow solid was slowly produced.

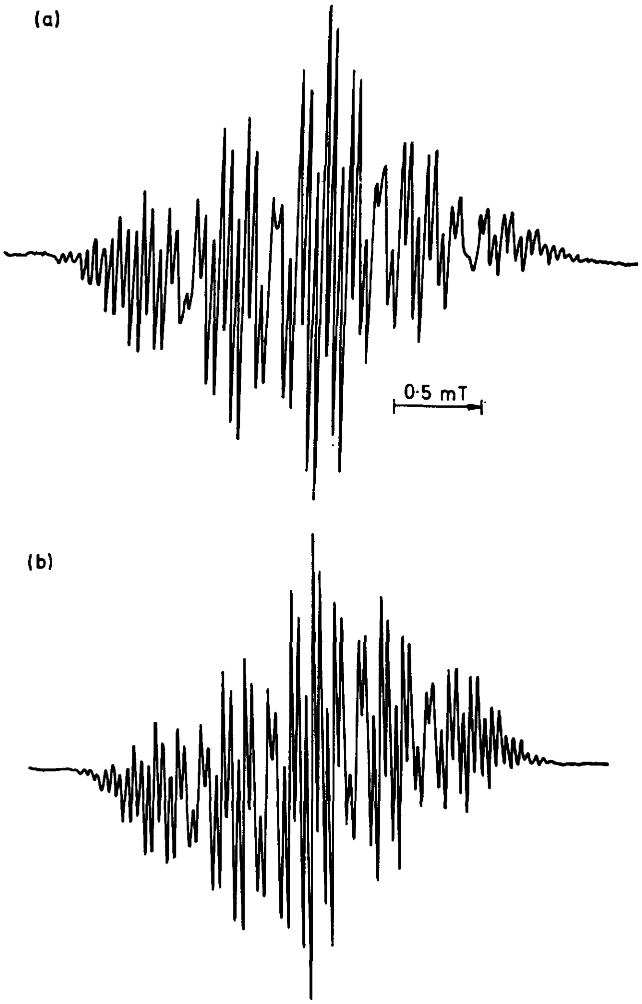


FIGURE 2 E.s.r. spectrum of $[S\{N(C_6H_4Me\text{-}4)\}_2]^-$ with K^+ gegenion in 1,2-dimethoxyethane solution at *ca.* 10 °C: (a) experimental, (b) simulated with parameters in Table 2 and line width = 0.03 mT

Reduction of $S(NC_6H_4X)_2$ with potassium gives the corresponding radical anions $[S(NC_6H_4X)_2]^-$ as green (X = 4-H or 4-Me) or deep purple (X = 4-NO_2) species with symmetrical e.s.r. spectra (Figure 2). No coupling to ^{39}K has been detected in these spectra. These aromatic di-imidosulphur anion radicals are stable for several hours at room temperature when X = H or Me, but slowly decompose giving more complex spectra, possibly consistent with radicals containing four ^{14}N atoms but not as yet fully characterised. The radicals with X = NO_2 decompose more readily.

Potassium reduction of deep purple solutions of $[M(CO)_4\{S(NBu^t)_2\}]$ (M = Cr, Mo, or W) in 1,2-dimethoxyethane produces brownish solutions with simple e.s.r. spectra characteristic of the anion radicals $[M(CO)_4\{S(NBu^t)_2\}]^-$. When M = Mo or W, these are stable for several hours and satellites arising from isotropic coupling with $^{95/97}Mo$ (25.38%) or ^{183}W (14.28%) are well defined. When M is Cr, the half-life of the radical is only *ca.* 6 min and other more complex e.s.r. spectra are also evident. Satellites due to ^{53}Cr (9.54%) are not well defined. The line widths of the main signals are such as to obscure any splitting by the ^1H atoms of the t-butyl groups (Figure 3).

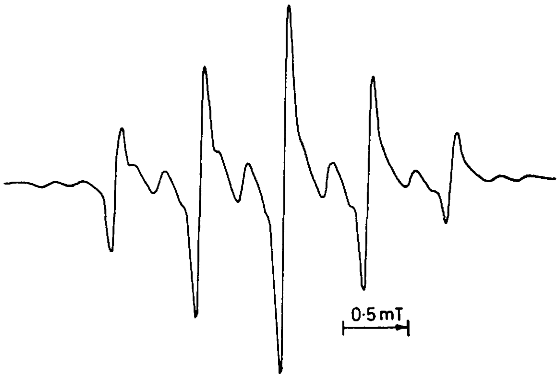


FIGURE 3 E.s.r. spectrum of $[Mo(CO)_4\{S(NBu^t)_2\}]^-$ with K^+ gegenion in 1,2-dimethoxyethane at *ca.* 10 °C

Attempts to prepare complexes $[M(CO)_4\{S(NPh)_2\}]$ by reaction of $S(NPh)_2$ with $[M(CO)_4(NCMe)_2]$ have proved unsuccessful, but mixing $[M(CO)_5(thf)]$ with $S(NPh)_2$ in thf at room temperature produces greenish solutions. With molybdenum, the product decomposes readily, but with chromium or tungsten green crystals, soluble in hexane, are obtained. Only in the case of chromium has it been possible to obtain a simple paramagnetic species by reduction of a 1,2-dimethoxyethane solution with a potassium mirror. The neutral chromium complex may tentatively be assigned the formula $[Cr(CO)_4\{S(NPh)_2\}]$ on the evidence of its mass spectrum [peaks at *m/e* corresponding to P^+, $(P - 3CO)^+$, $(P - 4CO)^+$, $S(NPh)_2^+$, and fragments], i.r. spectrum [ν(CO) in hexane: 2 022, 1 969, 1 957, and 1 900 cm^{-1}] and n.m.r. spectrum (δ = 7.5, complex band in $CDCl_3$). Hence the e.s.r. spectrum has been assigned to the corresponding radical anion. This assignment is supported by the similarity between the splitting pattern observed and that from the anion of *NN'*-diphenyldi-imidosulphur and also by the effects of complexation on $g_{iso.}$ and $A_{iso.}(^{14}N)$ when compared with the corresponding t-butyl species.

By computer simulation, various e.s.r. parameters have been fitted as well as possible to the observed spectra. Those for the several spectra derived from $S(NBu^t)_2$ are given in Table 1 and those for the aromatic species in Table 2.

In the first set, as well as values for $g_{iso.}$ and $A_{iso.}(^{14}N)$, $A_{iso.}$ values for ^{33}S, ^1H, and the gegenion are given for the simple reduction products, the value for ^{39}K being only an upper limit. For the Group 6A complexes, $A_{iso.}(M)$ values are given. In these complexes it is notable that the values for $g_{iso.}$ and $A_{iso.}(^{14}N)$ vary little from one complex to the next. They may be compared

TABLE 1

E.s.r. parameters[a] and unpaired electron densities at nitrogen atoms[b] for anion radicals derived from $S(NBu^t)_2$ in 1,2-dimethoxyethane at *ca.* 10 °C

Species	Gegenion(M^I)	$g_{iso.}$	$A_{iso.}(^{14}N)$	ρ^{π}_N	$A_{iso.}(M^I)$	$A_{iso.}(^{33}S)$[c]	$A_{iso.}(^1H)$	$A_{iso.}(M)$
$[S(NBu^t)_2]^-$	K^+	2.0071	0.515	0.23	*ca.* 0.005	0.92	0.024	
	Na^+	2.0072	0.51	0.23	0.07[d]	0.93	0.023	
	Li^+	2.0071	0.495	0.225	0.072	0.95	0.020	
$[Cr(CO)_4\{S(NBu^t)_2\}]^-$	K^+	2.0060	0.69	0.31				<0.1
$[Mo(CO)_4\{S(NBu^t)_2\}]^-$	K^+	2.0066	0.65	0.30				0.215
$[W(CO)_4\{S(NBu^t)_2\}]^-$	K^+	2.0080	0.65	0.30				0.40

[a] $A_{iso.}$ values in mT. Estimated errors: $g_{iso.}$ ±0.0005, $A_{iso.}$ ±0.005 mT unless stated otherwise. [b] Using $Q_N = 2.2$ mT. [c] Estimated error for $A_{iso.}(^{33}S)$ is ±0.03 mT. [d] At -50 °C, $A_{iso.}(^{23}Na) = 0.088$ mT.

TABLE 2

E.s.r. parameters[a] and unpaired-electron densities at nitrogen atoms[b] for anion radicals derived from $S(NR)_2$ (R = aryl group) with K^+ gegenions in 1,2-dimethoxyethane at *ca.* 10°C

				$A_{iso.}(^1H)$			
Species	$g_{iso.}$	$A_{iso.}(^{14}N)$	ρ^{π}_N	2,2′,6,6′	3,3′,5,5′	4,4′	CH_3
$[S(NPh)_2]^-$	2.0064	0.445	0.20	0.139	0.045	0.139	
$[S\{N(C_6H_4Me\text{-}4)\}_2]^-$	2.0063	0.444	0.20	0.140	0.046		0.143
$[S\{N(C_6H_4NO_2\text{-}4)\}_2]^-$	2.0064	0.361,[c] 0.031	0.16,[c] 0.014	0.124	0.031		
$[Cr(CO)_4\{S(NPh)_2\}]^-$	2.0050	0.542	0.25	0.145	0.048	0.150	

[a] $A_{iso.}$ in mT. Estimated errors: $g_{iso.}$ ±0.0005, $A_{iso.}$ ±0.005 mT. [b] Using $Q_N = 2.2$ mT. [c] Tentatively assigned to ^{14}N of N_2S group (see text).

with the values reported for other anions $[M(CO)_4L]^-$ (L = bipy[19] or RNCR′CR′NR[19,20]) (bipy = 2,2′-bipyridyl).

For the various aromatic species, results for $g_{iso.}$, $A_{iso.}(^{14}N)$, and $A_{iso.}(^1H)$ only are given. Assignment of the various values for ^1H for species derived from $S(NC_6H_4X)_2$ is unambiguous for X = H or Me if higher unpaired electron density is found at the 2,2′ and 6,6′ positions than at the 3,3′ and 5,5′ positions. Comparison with results for $[PhNNPh]^-$,[21] $[PhNO]^-$,[22] and PhNSPh[23] supports this contention. However, in the case where X = NO_2 ambiguity arises since two sets each of two magnetically equivalent ^{14}N atoms with four magnetically equivalent ^1H atoms are present. Only a tentative assignment is possible in this situation.

Unpaired electron densities at ^{14}N and ^{33}S atoms have been related to the corresponding $A_{iso.}$ values by equations (1) and (2), where the various Q's are coefficients and the various ρ^{π}_A are unpaired electron densities in π orbitals located at atom A. The coefficient of the third

$$A_{iso.}(^{14}N) = Q_N\rho^{\pi}_N + Q^N_{SN}\rho^{\pi}_S + Q^N_{CN}\rho^{\pi}_C \qquad (1)$$

$$A_{iso.}(^{33}S) = Q_S\rho^{\pi}_S + Q^S_{NS}\rho^{\pi}_{N_1} + Q^S_{NS}\rho^{\pi}_{N_2} \qquad (2)$$

term in equation (1) is small and ρ^{π}_C *ca.* 0, at least for aliphatic systems, so that this term may be neglected. It has also been proposed[8] that Q^N_{SN} is *ca.* 90 μT so that the second term in the equation may also be neglected. Hence we have equation (3) for the unpaired electron density at the nitrogen atoms of the NSN fragment.

$$\rho^{\pi}_N = A_{iso.}(^{14}N)/Q_N \qquad (3)$$

Values of Q_N in the neighbourhood of 2.2 mT have been suggested[7,8] and results for the various systems calculated with this parameter are presented in Tables 1 and 2.

In equation (2), a value of 3.3 mT has been suggested for Q_S in sulphur heterocyclic radicals,[24] where it has also been suggested that the other term of the equation may be neglected. We thus have equation (4) for the free electron density at the sulphur atom. Results calculated with the value of Q_S quoted above {*ca.* 0.28 in $[S(NBu^t)_2]^-$} appear to be too small, since not all the electron-spin density is accounted for, and a value of Q_S of 1.73 mT would appear to be required to fit the results for this radical.

$$\rho^{\pi}_S = A_{iso}(^{33}S)/Q_S \qquad (4)$$

Analysis of the frozen-solution spectrum of $K[S(NBu^t)_2]$ gives $g_{\parallel} = 2.002(4)$ and $g_{\perp} = 2.010(0)$, hence $g_{av.} = 2.007(4)$, in close agreement with $g_{iso.} = 2.007(1)$. The coupling constant $A_{\parallel}(^{14}N)$ is 1.46 ± 0.03 mT but the corresponding $A_{\perp}$ is not resolved. Using the relationship $3A_{iso.} = A_{\parallel} + 2A_{\perp}$ with $A_{iso.} = 0.515$ mT and assuming that $A_{iso.}$ and $A_{\parallel}$ have the same sign (taken as positive) gives $A_{\perp}$ as (+) 0.04 mT. $A_{aniso.}$ given by $A_{\parallel} - A_{iso.}$ is (+) 0.94 mT. For a single unpaired electron in a nitrogen $2p$ orbital $A_{aniso.} = 3.35$ mT.[25] Hence $\rho^{\pi}(2p)$ comes out as 0.28. This value is somewhat higher than, but not completely inconsistent with the unpaired electron density calculated from the isotropic data (Table 1).

Molecular Orbital Calculations.—A number of calculations by the CNDO/2[26] method have been reported for the neutral species $S(NR)_2$.[14,15] These have been extended to the various radical anions concerned in this work and to some related model compounds. The standard CNDO/2 program[27] has been used as a basis for these calculations, extended as recommended by Clack *et al.*[28] to deal with chromium atoms. In some cases, localised orbitals, obtained by the Trindle–Sinanoğlu[29] modification of the Edmiston–Ruedenberg [30] procedure, have been calculated with the program ORBLOC [31] in order to facilitate recognition of the location of the unpaired electron.

Since the INDO method [32] has supposed advantages for calculations of quantities such as e.s.r. parameters, it has been applied with the parameters due to Benson and Hudson [33] for the sulphur-atom *s* and *p* orbitals. Since no similar or related parameter values could be found for the *d* orbitals, these were either unchanged from those resulting from the general SCF procedure involved, or else omitted altogether. Their omission would be in line with the experimental findings of Bartetzko and Gleiter [34] for this type of compound and with the general results of Galasso [35] for INDO calculations of e.s.r. parameters of sulphur heterocycles.

In all cases without a metal atom, the geometry of the NSN fragment has been kept constant with the N–S distance 153 pm and the NSN angle 114°. Other bond lengths and angles have been taken from the CNDO/2 recommended set of Pople and Gordon.[36] The SNR angles have varied from 118° for the *E* configuration to 130° for the *Z* configuration at either end of the NSN fragment in planar configurations. For non-planar geometries a linear dependence of torsion angle and SNR bond angle has been assumed. For the calculations on $[Cr(CO)_4\{S(NR)_2\}]^-$ the geometry of the related tungsten compound [37] has been used for the surroundings of the central metal atom.

Calculations have been made for the three different planar conformations of the various radicals where such might reasonably exist. For some of the simpler radicals, calculations have also been made for non-planar configurations of the ions but these have indicated that, except in the case of the model compounds $[S(NH)_2]^-$ and $[S(NMe)_2]^-$, the planar configuration seems to be preferred. These ions seem to be twisted from the planar configurations, although the exact geometry depends on the method of calculation. Similar non-planarity for neutral $S(NMe)_2$ has been reported.[15] The studies of non-planar configurations also indicate that, whilst considerable flexibility exists, conversion from the *E*/*Z* conformation predicted for the neutral molecules [14,15] to the *E*/*E* arrangement which is apparently most stable for the anions is likely to be an irreversible process. The *E*/*E* conformation is also that to which the system will be constrained in the presence of a Group 6A metal to which it is attached as a bidentate ligand.

It is interesting to note that in the case of bis(4-methylphenylimido)sulphur, for which an *X*-ray structure has shown that the conformation is *E*/*Z* and the planes of the aromatic rings are twisted relative to one another,[12] the results calculated for the *E*/*Z* anion are virtually unaffected by this twist, being little altered if the anion is made effectively planar. The electron distribution around the atoms of the NSN group is thus, while not independent of the rest of the molecule, essentially asssociated with a molecular orbital localised in the vicinity of the three atoms and which, although of essentially π character, is apparently not greatly involved in conjugation with other molecular π orbitals which may be present.

Localised orbital calculations support this contention. The unpaired electron occupies an orbital largely concentrated on the sulphur atom and involving the adjacent nitrogen atoms to a lesser extent. The contributions from the sulphur *p* and *d* orbitals are such as to explain successfully the twisted geometry encountered with $HNSNH^-$ in the CNDO/2 calculations, although some other explanation has to be found for the corresponding twist in the structure suggested by the INDO calculations where *d* orbitals are absent.

TABLE 3

Total spin densities at nitrogen and sulphur atoms calculated by semi-empirical methods (the NSN conformation is *E*/*E* in all cases)

	CNDO/2			INDO with *d* orbitals		INDO without *d* orbitals	
Species	ρ_N	ρ_S	ρ_{Cr}	ρ_N	ρ_S	ρ_N	ρ_S
$[S(NH)_2]^-$	0.164	0.671		0.218	0.800	0.450	0.218
$[S(NMe)_2]^-$	0.157	0.672		0.209	0.874	0.475	0.248
$[S(NBu^t)_2]^-$	0.169	0.650		0.217	0.854		
$[S(NPh)_2]^-$	0.142	0.659		0.170	0.860		
$[S\{N(C_6H_4NO_2\text{-}4)\}_2]^-$	0.130 [a] −0.002 [b]	0.664		0.136 [a] −0.005 [b]	0.886		
$[Cr(CO)_4\{S(NH)_2\}]^-$	0.161	0.656	0.053				
$[Cr(CO)_4\{S(NMe)_2\}]^-$	0.167	0.610	0.085				

[a] N in N_2S group. [b] N in NO_2 group (the sign is not of real significance).

The unpaired electron densities for the nitrogen and sulphur atoms, and for the chromium atom where appropriate, calculated by the various procedures are given in Table 3.

None of the methods gives results for both ρ_N and ρ_S in reasonable agreement with the values derived from the experimental data, although with both CNDO/2 and INDO (with sulphur *d* orbitals) the trends in ρ_N are reproduced. Undoubtedly the best fit for ρ_N is obtained by the INDO method with *d* orbitals present. When these orbitals are removed from the basis set, the values for ρ_S become absurdly high whilst those for ρ_S become too low. In view of the uncertainty in the value for Q_S used to calculate ρ^{π}_S from the experimental data, and the presence of an excess of spin (of opposite sign) on other atoms, it may be that some alternative formula for calculating $\rho^{\pi}{}_{S}$ from experimental data is required to obtain a reliable value matching the theoretical predictions somewhat more closely.

DISCUSSION

The calculations on various molecules and radical anions and comparison with He(I) photoelectron spectra for various species $S(NR)_2$[14] show similar ordering of the molecular orbitals whether the molecule or ion is in the *E*/*E* or *E*/*Z* configuration. The l.u.m.o. for the various neutral molecules is apparently of π^* type and this is supported by the nature of the orbital containing the unpaired electron as deduced from the open-shell calculations, particularly with localisation. This orbital involves contributions from the sulphur and nitrogen atoms, including the 3*d* orbitals of sulphur if these are included in the basis set.

The one-electron reduction product is thus expected to be this π radical. Since the singly-occupied orbital is strongly antibonding, with a nodal plane in the vicinity of the sulphur nucleus, the barrier to conformer interchange in the radical anions is expected to be quite low; lower, at any rate, than that for the corresponding molecule. The calculations for $HNSNH^-$ indicate that for this simplest species, interconversion among the various conformations would indeed be facile but, for anions with bigger terminal groups, all the results indicate considerable resistance to change from the *E*/*E* conformation once this has been attained. It therefore seems likely that the absence of evidence from the e.s.r. spectra for the presence of more than one conformer is associated with the relatively high stability of this one planar configuration, rather than with free interconversion among a variety of conformers giving rise to a random mixture and an average signal.

The $[S(NBu^t)_2]^-$ *Ion*.—The e.s.r. spectrum of this anion indicates exact magnetic equivalence of the two nitrogen atoms. This is in accordance with the prediction of the *E*/*E* structure as most stable, the alternative symmetrical conformation (*Z*/*Z*) being excluded by steric phenomena. Calculations for the *E*/*Z* conformation indicate that different unpaired electron densities would be expected at the different nitrogen atoms, so that such a fixed structure would not fit the results. The alternative of a freely rotating system, giving rise to an average signal, is somewhat unlikely in view of the bulky nature of the t-butyl groups, which make arrangements in the neighbourhood of the *Z*/*Z* conformation virtually unattainable.

The interaction between alkali-metal gegenions and this radical anion appears to be small, but $A_{iso.}$ values for ^7Li and ^{23}Na indicate decreasing unpaired electron density in the respective metal valence-electron orbitals. [For the free atoms, $A_{iso.}(^7Li) = 10.3$ mT and $A_{iso.}(^{23}Na) = 22.4$ mT.[25]] The observed phenomena must reflect the decreasing co-ordinating tendency of the nitrogen sites to the metal ions as one goes from lithium to potassium.

Agreement between the calculated electron densities at the nitrogen atoms, based on the e.s.r. measurements (Table 1), and those derived from the various semi-empirical m.o. computations is not particularly good. Reasonable agreement between the experimental value at the nitrogen atoms and that for a nitrogen atom with *E* configuration is obtained for the INDO calculations with uncorrected *d* orbitals present, but no reasonable agreement is obtained for the sulphur atoms. On the other hand, in the m.o. results, which are total unpaired electron densities, there is significant unpaired density of opposite sign present at some of the atoms, so that the total density on the N and S atoms is sometimes quite far from the simple predicted value of 1.0.

The success of the experiments with $S(NBu^t)_2$ is interesting when contrasted with the complete failure to produce any radical anion from $S(NMe)_2$. It may be due to the presence of the bulky t-butyl groups impeding radical decomposition reactions or to the absence of β-hydrogen atoms which may be involved in a decomposition process of the $[S(NMe)_2]^-$ anion, if formed.

The $[S(NR)_2]^-$ *Ions* (R = *aryl group*).—Here again there is no evidence from the e.s.r. spectra to suggest that more than one conformer is present. Again the best agreement between the unpaired electron densities derived from e.s.r. measurements and the results of the m.o. calculations is obtained for the INDO method with *d* orbitals included. In these radicals, $A_{iso.}(^{14}N)$ and hence $\rho^{\pi}{}_{N}$ are somewhat lower than for $[S(NBu^t)_2]^-$ (Table 2). Certainly the results of the m.o. calculations show that some of the unpaired electron density is transferred from the NSN system to the 2, 4, and 6 positions of the rings.

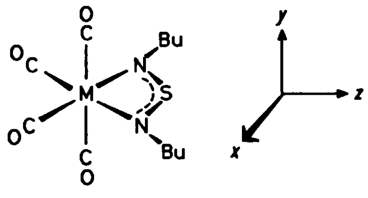
From the experimental results for $A_{iso.}(^1H)$, unpaired electron densities at the ring-carbon atoms can be calculated using relationship (5). With a value of Q_{CH} of

$$\rho^{\pi}{}_{C} = A_{iso.}(^1H)/Q^{H}{}_{CH} \qquad (5)$$

2.5 mT, the unpaired π-electron densities in the radicals $[S\{N(C_6H_4X\text{-}4)\}_2]^-$ are 0.056 at the 2,2′,6,6′ positions (X = H or Me), 0.018 at the 3,3′,5,5′ positions for the same species and, at the 4,4′ positions 0.056 (X = H) and 0.053 (X = Me, using $Q^{H}{}_{C\text{-}CH_3} = 2.7$ mT). The corresponding values for X = H from the m.o. calculations do not agree particularly well, although the trend is reproduced. The average values at the 2 (*etc.*), 3 (*etc.*), and 4,4′ positions obtained by the INDO method including *d* orbitals are 0.017, −0.024, and 0.024 respectively, the minus sign indicating that the phase of the unpaired spin is different at the 3,3′ and 5,5′ positions than at the others.

For the anion derived from bis(4-nitrophenylimido)-sulphur the presence of the nitro-groups seems to reduce the unpaired electron density at the nitrogen atoms of the NSN fragment still further. The ring densities seem to be little altered. The m.o. results indicate that this pattern is present there too. In particular they reveal that there is no significant accumulation of unpaired electron density at the nitrogen atoms of the nitro-groups, so that the uncertainty concerning the allocation of electron density previously alluded to is removed.

The $[\text{M(CO)}_4\{\text{S(NR)}_2\}]^-$ *Ions*.—An *X*-ray study of the crystalline neutral complex $[\text{W(CO)}_4\{\text{S(NBu}^t)_2\}]$ has shown it to have the structure (I) with the ligand in the



(I)

E/*E* conformation and approximately C_{2v} symmetry overall.[37] The NSN angle is 93.4°, much smaller than that for the free ligand (*ca.* 113°) and the N–S bonds are slightly lengthened, to *ca.* 159 pm, but still retain some double-bond character.

The radical anions $[\text{M(CO)}_4\{\text{S(NBu}^t)_2\}]^-$ (M = Cr, Mo, or W) with magnetically equivalent ^{14}N atoms and with Group 6A metal isotropic hyperfine coupling presumably retain the C_{2v} structure. In comparison with free $[\text{S(NBu}^t)_2]^-$ these complex radicals show an increase in $A_{\text{iso.}}(^{14}\text{N})$ of 28% (M = Mo or W) and 34% (M = Cr). This may reflect the change in hybridisation, as shown by the altered bond angles occurring on complexation, but could also arise from some spin polarisation of M–N σ bonds by unpaired spin density at the metal atom. A similar increase of $A_{\text{iso.}}(^{14}\text{N})$ of 22% is found on complexation of the diphenyldi-imidosulphur radical anion in $[\text{Cr(CO)}_4\{\text{S(NPh)}_2\}]^-$ and this has also been observed previously in anion radicals of complexes of diazabutadiene derivatives.[20]

The experimental $A_{\text{iso.}}(\text{M})$ values are low compared with typical values for Cr and Mo ($S = \frac{1}{2}$) in complexes with one unpaired electron in a d_{xy} orbital (*ca.* 2 and 5 mT respectively)[25] and the greater values which might be expected in the case of tungsten. Thus it may be postulated that the unpaired electron in $[\text{M(CO)}_4\{\text{S(NBu}^t)_2\}]^-$ is essentially ligand-based, with little metal *d*-orbital involvement and this is supported to some extent by the difference in energies of the b_2 orbital in $\text{S(NBu}^t)_2$[14] and the d_{yz} orbital in a C_{2v} M(CO)_4 fragment.[38]

However, Vrieze and co-workers[4b] have proposed, on the basis of charge-transfer bands, that in the neutral complexes metal-to-ligand π bonding involving overlap of metal *d* and ligand b_2 orbitals is strong, a contention that is supported to some extent by shifts of ν(CO) in the i.r. spectra.[3,4b] A possible explanation for the low $A_{\text{iso.}}(\text{M})$ values in the anions is that the isotropic coupling arising from a significant spin density at the metal is reduced by spin density at the nitrogen atoms. An equation such as (6) may be proposed, where Q_{M} is negative and Q^{M}_{MN} may be positive.

$$A_{\text{iso.}}(\text{M}) = Q_{\text{M}}\rho_{d_{yz}} + 2\,Q^{\text{M}}_{\text{MN}}\rho^{\pi}_{\text{N}} \qquad (6)$$

The results of our CNDO/2 m.o. calculations with localisation show that the orbital containing the unpaired electron is apparently quite tightly localised on the S atom. The calculated spin densities (Table 3) show little difference from those of free $[\text{S(NR)}_2]^-$.

The decomposition products of $[\text{Cr(CO)}_4\{\text{S(NBu}^t)_2\}]^-$ which appear to be radical anions containing four ^{14}N atoms may arise from a process related to the oxidative dimerisation of $[\text{Mo(CO)}_4(\text{dab})]^-$ (dab = diazabutadiene) to $[\text{Mo}_2(\text{CO})_6(\text{dab})_2]$.[39]

[9/950 *Received, 20th June*, 1979]

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