Electron Spin Resonance Investigation of Sulphur-33 and Nitrogen-15 Substituted Dithiazol-2-yl and Dithiazolidin-2-yl Free Radicals

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Received 5th August, 1982

Thermal cyclo-addition reactions of tetrasulphur dinitride with certain alkynes generate a new series of stable free radicals possessing the 1,3,2-dithiazolyl ring. The radicals have simple e.s.r. spectra and are potentially useful spin probes or labels. The sharpness of the spectral lines has enabled us to observe natural abundance lines from nitrogen-15, sulphur-33 and carbon-13. The presence of two equivalent sulphur atoms in the heterocyclic ring has been demonstrated by isotopic double labelling with nitrogen-15 and sulphur-33. An isotopic triple labelling experiment with the latter two isotopes and with deuterium was carried out with the related 1,3,2-dithiazolidinyl radicals. Temperature coefficients of coupling constants were measured for both classes of radicals and INDO calculations showed that nitrogen out-of-plane wagging is responsible for all the temperature coefficients.

Molecular orbital calculations were performed for the 1,3,2-dithiazolyl and 1,3,2-dithiazolidinyl structures using semi-empirical INDO and *ab inito* Gaussian 76 computer programs: the optimised structural parameters from both calculations are in good agreement. The INDO calculations gave signs and magnitudes of isotropic coupling constants in overall agreement with those observed experimentally.

We have reported previously¹⁻⁴ our discovery of a new class of free radicals which have the 1,3,2-dithiazolidin-2-yl structure:



where R_1 usually represents endo hydrogen atoms and R_2 represents the 1 and 4 carbon atoms of a norbornane ring. The radicals can be prepared either by photolysis of the adducts formed⁵ by tetrasulphur tetranitride and norbornenes or by thermal reaction of tetrasulphur dinitride with strained alkenes. The latter method is more efficient and radicals can be prepared from alkenes which do not form adducts with S_4N_4 . This method of radical production from thermal reactions of closed-shell molecules, particularly by cyclo-addition, is by no means common.⁶ We have shown⁷ that tetrasulphur dinitride can be labelled easily with sulphur-33 and/or with nitrogen-15, enabling the presence of two equivalent sulphur atoms in the dithiazolidinyl structure to be established.³ Substitution with nitrogen-15 is useful since it simplifies the e.s.r. spectrum and, by virtue of its larger hyperfine coupling constant, reduces the overlapping of lines.

We have found that some alkynes react thermally with tetrasulphur dinitride to give

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persistent free radicals which have e.s.r. parameters different from those of the dithiazolidin-2-yl radicals. One of the objects of this paper is to describe the elucidation of the structure of the radicals formed from alkynes because like the dithiazolidinyl radicals they could be useful spin probes or spin labels.⁸ Reactions of tetrasulphur tetranitride with electron deficient alkynes have been reported⁹ to give 3,4-disubstituted-1,2,5-thiadiazoles:

N // N // C -- C

(where $R = COOCH_3$, CN or CF₃) and/or a bicyclic compound:

More recently Tashiro et al.¹⁰ have found that refluxing S₄N₄ with phenylacetylene in toluene for 6 h gives products which include:

N N N N N N // // // // // Ph⁻C-C H Ph⁻C-C NH₂

They also found that methylpropiolate undergoes a similar reaction to give the products:

An aromatic heterocyclic free radical has been prepared¹¹ by reactions of orthosubstituted anilines with sulphur and bromine or chlorine. The radical was labelled with sulphur-33 and the e.s.r. spectrum indicated that two non-equivalent sulphur atoms are present. The suggested structure is:

R (),S

where R can be a variety of substituents.

Temperature coefficients of hyperfine coupling constants can provide useful information on intramolecular motion of radicals. We report here some coefficients which have been obtained for various nuclei in the radicals made from alkynes and from deuterated norbornene by reaction with tetrasulphur dinitride.





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EXPERIMENTAL

MATERIALS

Diphenylacetylene, diphenyldiacetylene and dimethylacetylene dicarboxylate were supplied by Aldrich Chemicals; hexafluorobut-2-yne came from Fluorochem Ltd; methylphenylacetylene was a gift from Mr J. Crabb. Acetylene dicarboxylic diamide was prepared using the method described by Blomquist and Winslow.¹²

Perdeuteronorbornene was prepared by the dehydrohalogenation method of Komppa and Beckman:¹³ we refluxed 0.3 g of 2-bromo-[${}^{2}H_{11}$]norbornane (98 atom % ${}^{2}H$: supplied by Merck, Sharp and Dohme, Canada Ltd) with 3 g of quinoline for 90 min at 270 °C. The resulting product weighed 0.1 g and was a 1:1 mixture of perdeuteronorbornene and perdeuteronor-tricyclene: the latter compound does not give a radical with tetrasulphur dinitride and hence a separation was unnecessary. Tetrasulphur dinitride was prepared⁷ by treating a solution of disulphur dibromide in carbon tetrachloride with ammonia gas until a pH of 8 resulted. The product was a mixture of tetrasulphur dinitride, tetrasulphur tetranitride and sulphur but only S₄N₂ gives radicals thermally. Small amounts (*ca.* 1 mg) of tetrasulphur dinitride labelled with 59.19 atom % sulphur-33 (from Oak Ridge National Laboratory) and with 98.6 atom % nitrogen-15 (from labelled ammonia supplied by Oriel Scientific Ltd) were prepared by the same method.⁷

RADICAL PREPARATION

Alkynes formed radicals with tetrasulphur dinitride in organic solvents in *ca.* 10% yield by allowing the reaction mixture to stand for several hours at room temperature. The exceptions were diphenylacetylene and diphenyldiacetylene which form radicals most efficiently in methanol containing a small amount of potassium hydroxide (*ca.* 10^{-5} %): higher concentrations of alkali destroy the tetrasulphur dinitride.

Dithiazolidinyl radicals were formed quickly from norbornene in most non-polar solvents.⁴

E.S.R. MEASUREMENTS

A Varian E-4 X-band e.s.r. spectrometer was used to obtain the spectra. Details of spectrometer calibration, g-factor measurements and computer simulations have been given previously.^{2, 4}

RESULTS

RADICALS FROM ALKYNES

Radicals were prepared from disubstituted alkynes having aromatic, alkyl, fluoroalkyl, amide or ester groups as substituents: radicals of this type could not be prepared from 1,4-dichlorobut-2-yne, acetylene dicarboxylic acid and but-2-yne. The but-2-ynes gave complex low-intensity e.s.r. spectra which we have not been able to analyse: impurities may be responsible for these radicals. Reactions of acetylene or hex-1-yne with tetrasulphur dinitride lead to weak signals which disappear rapidly and the major product is a high-molecular-weight solid.

The chemical properties of the radicals are markedly different from those of the dithiazolidin-2-yl radicals: (i) they do not react with oxygen, (ii) they are not photolysed at wavelengths of *ca*. 350 nm, (iii) they do not dimerise at low temperatures and (iv) they are stable in aqueous solutions at or above pH 8. Lack of reversible dimerisation and stability at high temperatures have enabled us to study the radicals in the temperature range from 155 to -110 °C.

The most likely structure for the radicals is that of a 1,3,2-dithiazole ring:



A similar structure has been proposed by Passmore and Schriver¹⁴ for the diamagnetic salt:



A partial proof of symmetry is that hexafluorobut-2-yne gives an e.s.r. spectrum⁸ containing splittings from six equivalent fluorine nuclei (see tables 1 and 2 for coupling constants). The other alkynes show simple spectra comprising three nitrogen lines which are very narrow; for example, the radical from diphenylacetylene has a low-field line width of only 0.028 mT in n-hexane at 21 °C: the spectra give these radicals good

Table	1.—Hyperfine	COUPLING	CONSTANTS	OF	THE	RADICAL	FROM	HEXAF	LUORO	but-2-	YNE
			AND	S_4	N_2						

solvent	temp./°C	$a^{N_{14}}/mT$	<i>a</i> ^{F19} /mT	
 CH,Cl,	-45.0	1.111	0.080	
2 2	-66.0	1.109	0.083	
	-85.5	1.107	0.086	
	-103.0	1.104	0.089	
CFCl,	-35.0	1.118	0.072	
o	-63.0	1.116	0.075	
	-102.2	1.109	0.075	

TABLE 2.—HYPERFINE COUPLING CONSTANTS OF THE RADICAL FROM HEXAFLUOROBUT-2-YNE AND S_4N_2 containing 98.6 atom % nitrogen-15 in CCl_4

temp./°C	<i>a</i> ^{N15} /mT	<i>a</i> ^{F19} /mT	<i>a</i> ^{S33} /mT
25.0	1.580	0.067	0.407
10.9	1.610	0.071	0.417
-6.1	1.569	0.069	0.415
-28.1	1.560	0.075	0.419



FIG. 1.-First-derivative e.s.r. spectrum at 21 °C of the free radical formed from diphenylacetylene and tetrasulphur dinitride in carbon tetrachloride. Satellite lines from sulphur-33 and nitrogen-15 are marked S and N, respectively.



FIG. 2.—First-derivative e.s.r. spectrum at 21 °C of the free radical formed from dimethylacetylene dicarboxylate and tetrasulphur dinitride, substituted with 59.19 atom % sulphur-33 and 98.6 atom % nitrogen-15, in dichloromethane. A is the experimental spectrum and B is the computed spectrum using a line width of 0.025 mT.

potential as spin probes or spin labels. The sharpness of the lines allows sulphur-33 (0.74 atom % abundance) and nitrogen-15 (0.37 atom % abundance) satellite lines to be resolved easily, as may be seen from fig. 1. Whilst such a spectrum proves the presence of sulphur in the radicals, the low natural abundance of sulphur-33 does not allow the number of sulphur atoms present to be deduced. For this reason we prepared a radical from dimethylacetylene dicarboxylate and tetrasulphur dinitride containing 59.19 atom % sulphur-33 (the maximum enrichment available). Substitution with 98.6 atom % nitrogen-15 was made simultaneously in order to expand and simplify the e.s.r. spectrum. Fig. 2 shows this spectrum along with a simulation which is based on the assumption that there are two equivalent sulphur atoms in the radical structure. The line heights are not reproduced well in the simulation because of asymmetric line broadening (see later): the high-field part of the spectrum is broadened by the nitrogen and the low-field section by the sulphur. The computed spectrum is a superimposition of the spectra from the six radical isotopomers containing the following abundances:

${}^{33}S^{15}N^{33}S$	34.51%
${}^{33}S^{15}N^{32}S$	47.62%
${}^{32}S^{15}N^{32}S$	16.46%
${}^{33}S^{14}N^{33}S$	0.49%
${}^{33}S^{14}N^{32}S$	0.67%
³² S ¹⁴ N ³² S	0.23%

solvent	temp./°C	$a^{N_{15}}/mT$	a^{S33}/mT
C ₆ H ₅ OCH ₃	100.0	1.557 ± 0.003	0.411 ± 0.003
5 5 5	80.0	1.559 ± 0.003	0.414 ± 0.003
	60.0	1.551 ± 0.004	0.413 ± 0.004
CH ₂ Cl ₂	21.0	1.553 ± 0.004	0.418 ± 0.007
	0.0	1.556 ± 0.004	0.421 ± 0.004
	-20.0	1.545 ± 0.005	0.425 ± 0.005
	-40.0	1.543 ± 0.005	0.422 ± 0.002
CFCl ₃	20.0	1.555 ± 0.003	0.413 ± 0.003
Ŭ	0.0	1.553 ± 0.003	0.417 ± 0.002
	-20.0	1.544 ± 0.003	0.417 ± 0.002
	-40.0	1.540 ± 0.008	0.417 ± 0.007
	-60.0	1.574 ± 0.005	0.424 ± 0.003
	-80.0	1.538 ± 0.008	0.421 ± 0.006
	-100.0	1.537 ± 0.007	0.426 ± 0.003

Table 3.—Hyperfine coupling constants of the radical from dimethylacetylene dicarboxylate and S_4N_2 containing 59.19 atom % sulphur-33 and 98.6 atom % nitrogen-15

Table 4.—Hyperfine coupling constants^a of the radical from dimethylacetylene dicarboxylate and S_4N_2 containing 98.6 atom % nitrogen-15

solvent	temp./°C	$a^{N_{15}}/mT$	<i>a</i> ^{N14} /mT	<i>a</i> ^{S33} /mT	<i>a</i> ^{C13} /mT
C ₆ H ₅ OCH ₃	155.0	1.557	1.112		
0 0 0	135.0	1.556	1.111	_	
	100.0	1.550	1.108	0.416	
	60.0	1.548	1.107	0.414	
	25.0	1.546	1.107		
CFCl ₃	-2.0	1.547	1.103	0.406	
0	-22.0	1.546	1.100	0.407	0.164
	-42.0	1.538	1.098	0.409	0.154
	-60.0	1.545	1.101	0.413	0.160
	-80.0	—	_		0.158
	-100.0	1.524	1.088	0.46	
	-110.0	1.520			
CH ₄ Cl ₉	20.2	1.541	1.101	0.415	0.153
	0.0	1.535	1.097	0.416	0.147
	-21.0	1.529	1.094	0.417	0.144
	-40.0	1.527	1.092	0.413	0.148
	-60.0	1.522	1.089	0.417	0.150
	-80.0	1.522	1.088	—	

 a Coupling constants for nitrogen-14, sulphur-33 and carbon-13 were measured from satellite lines.

The hyperfine coupling constants used for the simulation are those for dichloromethane at 21.0 °C listed in table 3. From the good match of the simulation it is clear that the radical contains two sulphur atoms and that these are equivalent; hence we propose that the radical contains the 1,3,2-dithiazolyl ring. Both this and the

solvent	temp./°C	$a^{N_{15}}/mT$	<i>a</i> ^{N14} /mT	<i>a</i> ^{S33} /mT
CCl4	34.2	1.494	1.182	0.443
1	21.7	1.502	1.071	0.392
	-17.8	1.516	1.180	0.400
СН₃ОН	22.1	1.480	—	0.399
CH ₃ OH containing	-20.0	1.485		0.386
10 ⁻⁵ % KOH	-60.4	1.480	_	0.407
	-89.1	1.485		

Table 5.—Hyperfine coupling constants^a of the radical from diphenylacetylene and S_4N_2 containing 98.6 atom % nitrogen-15

^a Coupling constants for nitrogen-14 and sulphur-33 were measured from satellite lines.



FIG. 3.—First-derivative e.s.r. spectrum of the free radical formed from dimethylacetylene dicarboxylate and tetrasulphur dinitride, substituted with 98.6 atom % nitrogen-15, in dichloromethane at 20.2 °C. Satellite lines from carbon-13, sulphur-33 and nitrogen-14 are marked C, S and N, respectively.

TABLE 6.—NITROGEN-14 HYPERFINE COUPLING CONSTANTS OF THE RADICAL	FROM
diphenylacetylene and $\mathbf{S_4N_2}$	•

solvent	temp./°C	<i>a</i> ^{N14} /mT	
$n-C_6H_{14}$	21.0 - 20.0 - 61.5 - 89.1	$1.113 \pm 0.001 \\ 1.104 \pm 0.002 \\ 1.102 \pm 0.006 \\ 1.094 \pm 0.001$	
CCl_4	$55.0 \\ 38.1 \\ 18.1 \\ 4.0 \\ -9.1 \\ -19.8 \\ 21.2 \\ -19.8 \\ 31.2 \\ -19.8 \\ 31.2 \\ -19.8 \\ 31.2 \\ -19.8 \\ 31.2 \\ -19.8 \\$	1.075 ± 0.003 1.075 ± 0.003 1.070 ± 0.002 1.117 ± 0.006 1.066 ± 0.007 1.063 ± 0.005 1.055 ± 0.015 1.055 ± 0.012	
CH ₃ OH containing 10 ⁻⁵ % KOH	$ \begin{array}{r} -31.2 \\ 27.4 \\ -4.0 \\ -30.7 \\ -53.9 \\ \end{array} $	$\begin{array}{c} 1.050 \pm 0.012 \\ 1.057 \pm 0.001 \\ 1.560 \pm 0.004 \\ 1.056 \pm 0.004 \\ 1.056 \pm 0.006 \end{array}$	

alkyne	solvent	temp./°C	<i>a</i> ^{N14} /mT
MeOOCC≡CCOOMe	CHCl3	$21.7 \\ -20.0 \\ -60.0 \\ -80.0$	$\begin{array}{c} 1.098 \pm 0.006 \\ 1.090 \pm 0.003 \\ 1.087 \pm 0.009 \\ 1.086 \pm 0.008 \end{array}$
MeOOCC=CCOOMe	none	$22.0 \\ -40.0 \\ -60.0 \\ -80.0 \\ -100.0$	$\begin{array}{c} 1.091 \pm 0.002 \\ 1.085 \pm 0.003 \\ 1.087 \pm 0.006 \\ 1.082 \pm 0.002 \\ 1.081 \pm 0.009 \end{array}$
$(CONH_2)C\equiv CCONH_2$	$CH_{3}OH + 10^{-5}\% KOH$	20.0 24.8 53.8	$\begin{array}{c} 1.097 \pm 0.001 \\ 1.099 \pm 0.001 \\ 1.097 \pm 0.008 \end{array}$
PhC≡C−C≡CPh	$Ch_3OH + 10^{-5}\%$ KOH	50.8 20.0 59.0 85.1	$\begin{array}{c} 1.076 \pm 0.007 \\ 1.082 \pm 0.008 \\ 1.065 \pm 0.008 \\ 1.063 \pm 0.007 \end{array}$
PhC≡CMe	n-C ₆ H ₁₄	$21.7 \\ -20.0 \\ -65.0 \\ -92.5$	$\begin{array}{c} 1.108 \pm 0.013 \\ 1.107 \pm 0.009 \\ 1.100 \pm 0.002 \\ 1.093 \pm 0.001 \end{array}$

TABLE 7.—NITROGEN-14 HYPERFINE COUPLING CONSTANTS OF THE RADICALS FROM ALKYNES AND S_4N_2

1,3,2-dithiazolidinyl structure are virtually unknown,¹⁵ even in closed-shell form, and thus the cyclo-addition reaction reported here could be an important synthetic route to these heterocycles.

We prepared 1,3,2-dithiazol-2-yl radicals with different substituents and, by using S_4N_2 substituted with nitrogen-15, we were able to obtain sulphur-33 coupling constants for a range of solvents at various temperatures (tables 4 and 5). As may be seen from fig. 3, carbon-13 satellites could also be resolved in some intances. Some nitrogen-14 coupling constants are collected in tables 6 and 7.

1,3,2-dithiazol-2-yl radicals have g-factors of 2.0064 ± 0.0001 , which is within experimental error of those (2.0065 ± 0.0001) found^{2.3} for 1,3,2-dithiazolidin-2-yl radicals.

1,3,2-DITHIAZOLIDIN-2-YL RADICALS

Lowering the temperature of some of these radicals to ca. -60 °C sharpens the lines in their e.s.r. spectra.⁴ We ascribed this to a reduction in intramolecular motion and in particular to that of out-of-plane bending of the dithiazolidine ring about the sulphur-sulphur axis. A possible way to prove this supposition is to obtain the temperature dependence of the sulphur hyperfine coupling constants. Since the dithiazolidinyl radicals have e.s.r. spectra with a great deal of resolved or unresolved fine structure, natural abundance sulphur-33 satellites are not as easily discerned as they are for the dithiazolyl radicals. As already demonstrated, sulphur-33 labelling is a simple matter but the choice of norbornene requires careful consideration. In establishing the structure of the radicals we prepared sulphur-33 versions with the norbornenes; 1,4-dimethoxybenzonorbornadiene² and exo,exo-5,6-dideuteronor-

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FIG. 4.—Second-derivative e.s.r. spectrum at -36.0 °C of the free radical formed from norbornene substituted with 98 atom % deuterium and tetrasulphur dinitride substituted with 59.19 atom % sulphur-33 and 98.6 atom % nitrogen-15 in dichloromethane. A is the experimental spectrum and B is the computed spectrum using a line width of 0.05 mT.

temp./°C	a ^{N15} /mT	<i>a</i> ^{s33} /mT	a ^{H2} /mT
30.0	1.831 ± 0.004	0.298 ± 0.004	0.051 ± 0.003
17.5	1.825 ± 0.014	0.292 ± 0.010	0.052 ± 0.003
11.3	1.827 ± 0.011	0.287 ± 0.003	0.051 ± 0.001
3.7	1.828 ± 0.016	0.294 ± 0.008	0.051 ± 0.003
-17.5	1.826 ± 0.014	0.296 ± 0.010	0.052 ± 0.001
-28.7	1.819 ± 0.015	0.293 ± 0.008	0.052 ± 0.002
-36.0	1.827 ± 0.013	0.300 ± 0.009	0.052 ± 0.002
- 53.0	1.810 ± 0.014	0.299 ± 0.020	0.052 ± 0.002
-66.8	1.808 ± 0.017	0.299 ± 0.010	0.052 ± 0.002
-85.8	1.809 ± 0.012	0.305 ± 0.012	0.053 ± 0.002

Table 8.—Hyperfine coupling constants of the radical from 98 atom % deuterated norbornene and S_4N_2 containing 59.19 atom % sulphur-33 and 98.6 atom % nitrogen-15, in CH_2Cl_2

born-2-ene.³ Neither of the radicals prepared from these 2:2:1-bicycloheptenes is suitable for measuring the temperature dependence of a^{S33} : the former radical is relatively large and hence the e.s.r. spectrum exhibits severe asymmetric line broadening² even at room temperature and both radicals have complex e.s.r. spectra, having $a^{833} \approx a^{H}$. In order to get sharper lines (that is to minimise all unresolved coupling) and to reduce the number of lines while at the same time expanding the spectrum, we prepared a radical from 98 atom % deuterated norbornene and tetrasulphur dinitride substituted with 98.6 atom % nitrogen-15 and 59.19 atom % sulphur-33. The second derivative of the best resolved spectrum we obtained is shown in fig. 4 along with a computer simulation using the first five isotopomer concentrations listed previously for the dithiazolyl radicals. It is not necessary to take into account contributions from hydrogen-1 because although the highest isotopomer concentration containing a proton is 0.97%, only hydrogens in position R₁ can affect the spectrum⁴ ($a_{R_1}^{H} = 0.34 \text{ mT}$) by providing resolvable lines: thus the concentration of hydrogen-1 in this position is 0.19%, which can be neglected. E.s.r. spectra were obtained over the temperature range from 30 to -86 °C and the hyperfine coupling constants derived from them are given in table 8.

MOLECULAR ORBITAL CALCULATIONS

In an attempt to rationalise the structures we propose, molecular orbital calculations were carried out using a Gaussian 76 computer program¹⁶ using a STO-3G basis set and an INDO program based on that devised by Pople¹⁷ and modified¹⁸ to allow its use with second-row elements. In order to save computer time, two hydrogen atoms were used as substituents. From table 9 it may be seen that both types of calculation give reasonable agreement for the optimum bond lengths and angles. A gratifying feature of the results is that the carbon–carbon bond length for the 1,3,2-dithiazolyl structure is shorter than that for 1,3,2-dithiazolidinyl.

The programs were also used to calculate spin densities and hyperfine coupling constants but only the INDO program gave reasonable values for a^{N14} . This is probably because the Gaussian 76 calculation does not 'spin annihilate' contributions to spin density from higher multiplicity spin states¹⁹ and therefore gives artificially high spin densities.²⁰ Table 10 lists the results obtained from the INDO program. The latter uses a semi-empirical factor to convert 1s orbital spin densities into isotropic coupling constants: the factors used for first-row elements are those suggested by Pople

	bond lengths/nm		bond angles/°		
hypothetical radical	INDO	Gaussian 76	INDO	Gaussian 76	
	C—S 0.185	C—S 0.180	CCS 113.5	CCS 114.5	
	S—N 0.172	S—N 0.171	CSN 101.1	CSN 100.9	
	C=C 0.136	C=C 0.130	SNS 110.8	SNS 109.2	
	C—S 0.184	C—S 0.181	CCS 112.0	CCS 110.5	
	S—N 0.173	S—N 0.176	CSN 102.4	CSN 106.5	
	C—C 0.150	C—C 0.154	SNS 111.2	SNS 105.9	

TABLE 9.—OPTIMISED	BOND	ANGLES	AND	BOND	LENGTHS	FOR	DITHIAZOLYL	AND
DITHIAZOLIDINYL RADICALS								

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alkvne or alkene			nucleus		
reacted with S_4N_2	14N	33 S	13C	19F	H_1
dimethylacetylene dicarboxylate	1.115 (1.101)	0.0474 (0.414)	-0.035 (0.149)		
acetylene dicarboxylic acid diamide	1.115 (1.097)	0.0474 (—)	-0.031 ()		
phenyl methyl acetylene	1.113 (1.107)	0.0474 (—)	-0.020 (Ph) () -0.047 (Me) ()		~ 0 (Ph) ^a 1.0167 (Me) ^a
perfluorobut-2-yne	1.124 (1.118)	0.0474 ()	-0.045 ()	-0.072 (0.075)	
norbornene ^b	1.111 (1.291)	0.0474 (0.298)	-0.347(0.33)	ļ	0.038 (0.346)

et $al.^{21}$ while the factor for sulphur-33 was obtained in a similar manner using 31 experimental values of a^{S33} . The factor for sulphur was found to be 237 ± 23 mT, which is considerably larger than that of 137 mT derived by Galasso²² for a series of dithiin cation radicals. The data in table 10 show that the INDO calculations correctly predict that the nitrogen hyperfine coupling constant is scarcely affected by substituents. They also predict that hydrogen coupling constants for the dithiazolyl radicals are smaller than the line width (ca. 0.028 mT). By contrast, a fluorinated methyl group is expected (as found) to give a measureable fluorine coupling constant. Unfortunately, using either method the calculations of sulphur and of carbon coupling constants do not give values in agreement with the observed ones.

SPIN DENSITIES FROM Q values

The 1,3,2-dithiazolyl ring can be regarded as being made up of five sp^2 hybridized atoms with the unpaired spin being located solely in a π molecular orbital. The latter is constructed from the five p_z atomic orbitals. In the following treatment we shall regard the radical as having carbon-centred substituents:



It has been shown²³ that when the unpaired spin is localised on a nitrogen atom in an aromatic free radical we can write:

$$a^{\mathrm{N}14} = Q^{\mathrm{N}14}\rho_{\mathrm{N}}$$

where $Q^{N_{14}}$ lies in the range 1.9-2.1 mT.^{24, 25} Thus, using an average of our values for a^{N} , the spin density, ρ_{N} , has a value of 0.56 ± 0.03 .

For the spin density localised on sulphur, ρ_s , an expression similar to that used by Goldberg *et al.*²⁶ is applicable:

$$a^{\mathrm{s}} = Q^{\mathrm{s}}_{\mathrm{s}}\rho_{\mathrm{s}} + Q^{\mathrm{s}}_{\mathrm{Ns}}\rho_{\mathrm{N}} + Q^{\mathrm{s}}_{\mathrm{Cs}}\rho_{\mathrm{C}}.$$

Using the Goldberg *et al.*²⁶ value of 4.03 mT for $Q_{\rm S}^{\rm S}$ and neglecting²⁷ $Q_{\rm NS}^{\rm S}$ and $Q_{\rm CS}^{\rm S}$, we find that $\rho_{\rm S} = 0.10$.

The full expression for the carbon-13 hyperfine coupling constant is:

$$a^{\mathrm{C}} = (S^{\mathrm{C}} + 2Q^{\mathrm{C}}_{\mathrm{CC'}} + Q^{\mathrm{C}}_{\mathrm{CS}})\rho_{\mathrm{C}} + Q^{\mathrm{C}}_{\mathrm{SC}}\rho_{\mathrm{S}} + Q^{\mathrm{C}}_{\mathrm{C'C}}\rho_{\mathrm{C'}}.$$

We can assume that $-Q_{\rm SC}^{\rm C} \approx Q_{\rm CS}^{\rm C} \approx Q_{\rm CC'}^{\rm C}$ and by symmetry $\rho_{\rm C} = \rho_{\rm C'}$. Hence, $a^{\rm C} = (S^{\rm C} + 3Q_{\rm CC'}^{\rm C} + Q_{\rm C'C}^{\rm C}) \rho_{\rm C} - Q_{\rm CC'}^{\rm C} \rho_{\rm S}$.

Karplus and Fraenkel²⁸ have proposed values of -1.27, 1.44 and -1.39 mT for $S^{\rm C}$, $Q^{\rm C}_{\rm CC'}$ and $Q^{\rm C}_{\rm C'C}$, respectively, and we calculate that $\rho_{\rm C} = 0.18$. It may be seen that the total spin density amounts to 1.0, which is satisfactory considering some of the assumptions made. Unfortunately, a similar calculation cannot be justified for the 1,3,2-dithiazolidinyl radicals since the ring system contains two single-bonded sp^3 hybridised carbon atoms.

Another approach can be used for the nitrogen spin densities since we have obtained⁸ nitrogen anisotropic coupling constants from the powder spectra of dithiazolyl dithiazolidinyl radicals. These data enable us to separate the s and p contributions to the spin densities on these nuclei, namely

$$\rho_{\rm s} = a^{\rm N}/A^{\rm o}$$
$$\rho_{\rm p} = (A^{\rm N}_{\rm zz} - a^{\rm N})/2B^{\rm o}$$

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where A° (= 55.51 and -77.87 mT, respectively, for nitrogen-14 and nitrogen-15) is the *s* Hartree–Fock atomic wavefunction and $2B^{\circ}$ (= 3.324 and -4.662 mT, respectively, for nitrogen-14 and nitrogen-15) are the *p* Hartree–Fock atomic wavefunctions.²⁹ From radicals containing either nitrogen-14 or nitrogen-15 we obtain the following spin density values:

dithiazolyl	dithiazolidinyl
$ ho_{ m s}^{ m N} = 0.019 \pm 0.001$	$\rho_{\rm s}^{\rm N} = 0.024 \pm 0.001$
$\rho_{\rm p}^{\rm N} = 0.51 \pm 0.01$	$\rho_{\rm p}^{\rm N} = 0.59 \pm 0.01$

DISCUSSION

LOW- AND HIGH-FIELD BROADENING IN THE E.S.R. SPECTRA

From fig. 3 and 4 it is clear that the e.s.r. spectra of both the dithiazolyl and the dithiazolidinyl radicals exhibit high-field broadening from the nitrogen nuclei and low-field broadening from the sulphur-33 nuclei. Fraenkel³⁰ and Sullivan and Brette³¹ have developed a qualitative treatment for predicting line width asymmetry for axially symmetric systems, namely

$B = \alpha a_i b_i \rho g^{(0)}$

where B is positive for high-field broadening and negative for low-field broadening, α is a positive constant if the magnetogyric ratio of nucleus *i* is positive, a_i is the isotropic coupling constant, b_i is related to the anisotropic hyperfine tensor (namely $A_{\parallel} - a_i$) and is taken to be negative for nuclei such as ¹³C, ¹⁴N and ¹⁷O and positive for protons, ρ is the π spin density for nuclei other than protons (for which the sign of the spin density on the proximate atom is taken), and $g^{(0)}$ is a function of the anisotropic g tensors, namely $6^{-\frac{1}{2}}[2g_z - (g_x + g_y)]$. For the nitrogen nucleus, α and ρ are known to be positive, b_i is negative and we have shown previously⁸ that $g^{(0)}$ is negative, hence the isotropic hyperfine coupling constant a^{N} must be positive. The situation for sulphur-33 is not so straightforward because the spin density is small and therefore could be either sign. For a simple sulphur-centred radical like PhS, $g^{(0)}$ is negative³² and thus taking b_i to be negative the product $a_i \rho$ is negative. In principle, the sign of a_i could be found from ENDOR measurements but sulphur-33 has not yet been observed³³ by ENDOR in solution. However, since π spin densities are generally much larger than σ spin densities (represented by a_i), it is likely that ρ_i is positive and a_i is negative for sulphur. This conclusion is not in agreement with the INDO calculations (see table 10) which predict that a^{S33} is positive.

EFFECT OF TEMPERATURE ON THE ISOTROPIC HYPERFINE COUPLING CONSTANTS

The INDO calculations enabled us to examine the effect of molecular vibrations on the coupling constants. We chose as our model the radical prepared from hexafluorobut-2-yne and tetrasulphur dinitride since this radical is relatively simple and we have measured temperature coefficients for three different coupling constants. The four lowest energy vibrational modes of this molecule are (i) out-of-plane motion of the nitrogen atom about the sulphur–sulphur axis, (ii) scissor motion of the two CF₃ groups, (iii) symmetric out-of-plane wagging of the two CF₃ groups and (iv) asymmetric out-of-plane wagging of the two CF₃ groups. Fig. 5 shows the variation of the total energy with displacement of atoms or groups for these four modes. Fig. 5 shows that the nitrogen out-of-plane bending is the most temperature sensitive. Calculation of the effect of this motion on the fluorine, nitrogen and sulphur coupling constants predicts that an increase in temperature reduces the magnitude of $a^{\rm F}$



FIG. 5.—Total energy against displacement from optimum energy positions of the 4,5-di(trifluoro)methyl dithiazolyl radical for the vibrational modes: (A) nitrogen out-of-plane bending, (B) CF₃ scissoring, (C) symmetric CF₃ wag and (D) asymmetric CF₃ wag.

and raises the magnitude of a^{N} and a^{S} . The latter prediction must be viewed with some doubt since the calculated and experimental values of a^{S} are not in accord (see table 10). The data contained in tables 2-4 and 8 do indicate that the magnitude of a^{S} decreases with temperature, thus suggesting that a^{S} is negative.

The data for the fluorine coupling constants are all in agreement: the INDO calculation predicts the sign to be negative (table 10) and experimentally the magnitude decreases with temperature (tables 1 and 2). A similar satisfactory situation occurs for the nitrogen coupling constants.

We carried out a similar analysis for the 1,3,2-dithiazolidinyl radical by considering two vibrational modes: (i) out-of-plane bending of the nitrogen atom about the sulphur-sulphur axis and (ii) bending of the entire heterocyclic ring about the internuclear axis of the 2 and 3 carbons of the norbornane ring. Once again the nitrogen out-of-plane motion was found to have the lower energy and the same predictions for the temperature dependence of the nitrogen and sulphur coupling constants were obtained.

Reddoch *et al.*³⁴ have carried out a vibrational analysis on aromatic free radicals and they have demonstrated how the temperature coefficient of the aromatic hydrogen coupling constant, a^{H_1} , can be related to a^{H_1}/a^{H_2} . From their data, Sullivan and Brette³¹ have derived the relationship:

$$\frac{a^{\rm H1}}{a^{\rm H2}} = 9.2 \times 10^{-3} \left(\frac{10^5}{a^{\rm H1}} \frac{\mathrm{d}a^{\rm H1}}{\mathrm{d}T}\right) + 6.5144$$

where 6.5144 is the hydrogen magnetogyric ratio divided by that of deuterium: most observed values of $a^{\rm H1}/a^{\rm H2}$ are < 6.5144. Taking values of $a^{\rm H2}$ from table 8 and comparing them with $a^{\rm H1}$ values we have obtained previously⁴ for radicals derived from norbornene, we calculate that $a^{\rm H1}/a^{\rm H2}$ is 6.63 and 6.62, respectively, for temperatures of 17.5 and -85.8 °C. We have also measured $a^{\rm H1}$ and $a^{\rm H2}$ in the same e.s.r. spectrum of the radical made from tetrasulphur dinitride and norbornene substituted with 98 atom % deuterium. In this spectrum hydrogen-1 satellite lines appear from hydrogen in one of the R₁ positions: good resolution was seen in the spectrum at a temperature of -66.4 °C with dichloromethane as solvent. The splitting constants are 0.355 and 0.053 mT giving a value for $a^{\text{H}1}/a^{\text{H}2}$ of 6.70. Substitution of these values into the above relationship gives a value of $-(5.2 \pm 1.7) \ 10^{-5} \ \text{mT K}^{-1}$ for $da^{\text{H}1}/dT$, if $a^{\text{H}1}$ is assumed to be negative. However, we have already established⁴ experimentally that this temperature coefficient is $-(8 \pm 2) \times 10^{-5} \ \text{mT K}^{-1}$, thus confirming that $a^{\text{H}1}$ is negative: from table 10 it may be seen that the INDO calculations also predict this negative sign.

NON-AROMATICITY OF THE 1,3,2-DITHIAZOLYL RING

Both experimental and INDO results show that substituents have little effect on the hyperfine coupling constants of dithiazolyl radicals. This suggests that there is no appreciable delocalisation of unpaired spin density or of charge from the heterocyclic ring on to the substituents. Further support for this contention comes from Gaussian 76 calculations of the charge distibution for the radical having two trifluoromethyl groups as substituents and we calculated the following charges on the indicated atoms to be

nitrogen	7.3244
sulphur	15.7136 (×2)
carbon (ring)	6.1343 (×2)
carbon (substituent)	5.5351 (×2)
fluorine	9.1516 (×6)

The total ring charge amounts to 51.0202 compared with the expected 51.0000: when two methyl groups are the substituents the ring charge totals 51.1134. These calculations show that the electronegativities of substituent groups have a minor effect on the ring charge distribution.

Additional evidence for the lack of aromaticity comes from a consideration of the experimental isotropic hyperfine coupling constants for the non-cyclic radical³ $C_6H_5SNSC_6H_5$, which has the values $a^{N14} = 1.14$ and $a^{S33} = 0.371$ mT. These values are remarkably similar to those observed for the dithiazolyl radicals.

The large g-factors found for our radicals do suggest³⁵ that there is partial delocalisation in the S—N—S fragment of the heterocyclic ring.

We thank the S.E.R.C. for providing a research assistantship for S.A.F. and a maintenance grant for R.S.P.

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