Cycloaddition Reactions of [SNS][AsF$_6$] with Potassium Tricyanomethanide†

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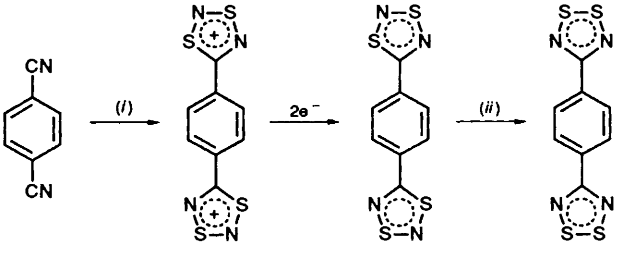
The reactions of 1, 2 and 3 equivalents of [SNS][AsF$_6$] with K[C(CN)$_3$] in liquid SO$_2$ generated three cycloaddition products $(NC)_2C\overline{CNSNS}$ **1**, $[(NC)C(\overline{CNSNS})_2][AsF_6]$ **2** and $[C(\overline{CNSNS})_3][AsF_6]_2\cdot SO_2$ **3**. These were characterised by IR spectroscopy, cyclic voltammetry and elemental analysis. Compounds **1** and **3** were further characterised by ^{14}N and ^{13}C NMR, UV/VIS spectroscopy, X-ray crystallography and (for **1**) mass spectroscopy. Compound **1** crystallises as polymeric sheets of dithiadiazole units held together through CN ··· S interactions and with a dihedral angle of 117.3° between planes. Compound **3** shows three equivalent $\overline{CNSNS}$ rings attached to a central carbon atom, the dication possessing C_{3h} symmetry. Molecular orbital calculations were used to deduce a probable reaction mechanism.

Studies of the facile cycloaddition reactions of [SNS]$^+$ with unsaturated centres (especially C≡C[1], C=C[2] and C≡N[3]) have recently been extended to multifunctonal systems[4] *e.g.* di- and tri-cyanobenzenes. The products are usually obtained with recovered yields in excess of 75%, with many reactions essentially quantitative. Reductions of the bis and tris 1,3,2,4-dithiadiazolium salts yield the analogous free-radical dithiadiazoles[4] (see Scheme 1). The lower solubility of these dithiadiazoles has allowed their isolation in high yield. Their photochemical rearrangement to the 1,2,3,5 isomer is readily monitored by ESR spectroscopy.

Recently[4a] we prepared {by reduction of the corresponding dication, $[p\text{-}C_6H_4(\overline{CNSNS})_2]^{2+}$} 5,5′-(1,4-phenylene)bis-(1,3,2,4-dithiadiazole), $p\text{-}C_6H_4(\overline{CNSNS})_2$. The solid, which is an insulator, contains a polymeric array of neutral molecules interacting through secondary S ··· N contacts and is the first (to our knowledge) extended system based on the thiazyl radical. Unlike most dithiadiazole radicals this material is only slightly air-sensitive (surviving for days in the atmosphere) and does not readily rearrange photochemically. It is indefinitely stable in the solid state (under normal illumination). Consequently we have continued to examine high-symmetry conjugated multiradicals as possible precursors to organic metals.

Many workers have used radicals as molecular building blocks for the formation of low-dimensional materials with novel electrical and magnetic properties. Of particular interest have been multiradicals with trigonal or higher symmetries, *e.g.* multicyanohydrocarbons[5] and 1,3-dithiol-2-ylidines.[6] Oakley and co-workers[7] have also prepared low-dimensional molecular conductors based on the use of thiazyl radicals (*e.g.* $CN_2S_2^{\bullet}$ and $CN_3S^{\bullet}$ rings as molecular building blocks for polymeric arrays of radicals.

There has also been much interest in the development of free-radical materials (particularly those possessing a three-fold axis of symmetry) in the preparation of organic magnets.[8] It has been proposed that the higher symmetry of these systems may stabilise the triplet/multiplet ground state required for possible ferro- or ferri-magnetism to occur.[9] Other research groups[10] have concentrated on nitroxide radicals, but these require bulky substituents to protect the =N–O$^{\bullet}$ functionality which, by necessity, limits the degree of secondary interaction between adjacent molecules. Consequently the possibility of co-operative magnetic interaction is greatly reduced. In dithiadiazoles, however, delocalisation helps to stabilise the radicals and no steric-protection groups are required, thus enhancing the possibility and extent of secondary interaction.



Scheme 1 5,5′-Phenylenebis(dithiadiazole/ium) system. (*i*) 2[SNS]$^+$; (*ii*) *hν* or heat

We have therefore studied the sequential reactions of [SNS][AsF$_6$] with the D_{3h} species [C(CN)$_3$]$^-$, as a route to possible precursors to such organic metals. We also studied the products by means of PM3 molecular orbital calculations and single-crystal X-ray crystallography.

Results and Discussion

Upon condensation of SO$_2$ on to the various stoichiometric mixtures of [SNS][AsF$_6$] and K[C(CN)$_3$] (1:1, 2:1 and 3:1), at liquid-nitrogen temperatures, an immediate deep purple colour was observed, later found to be indicative of the formation of the neutral 1:1 cycloaddition compound **1** (see Scheme 2). The 1:1 reaction (formation of **1**) was complete within minutes, yields of **1**–**3** (60–80%) being similar to those found for the reactions of [SNS]$^+$ with $C_6H_4(CN)_2$ and $C_6H_3(CN)_3$.[4a,b] After overnight reaction the corresponding 2:1 and 3:1 mixtures gave the red solids **2** and **3** (respectively), **3** crystallising as an SO$_2$ solvate from liquid SO$_2$. All three materials appear stable to the atmosphere for several hours (as shown by their appearance and relatively unchanged IR spectra) although **3** slowly gives up SO$_2$ of solvation upon standing [$\nu_{max}(SO_2)$: 528 and 1150 cm^{-1}].[11]

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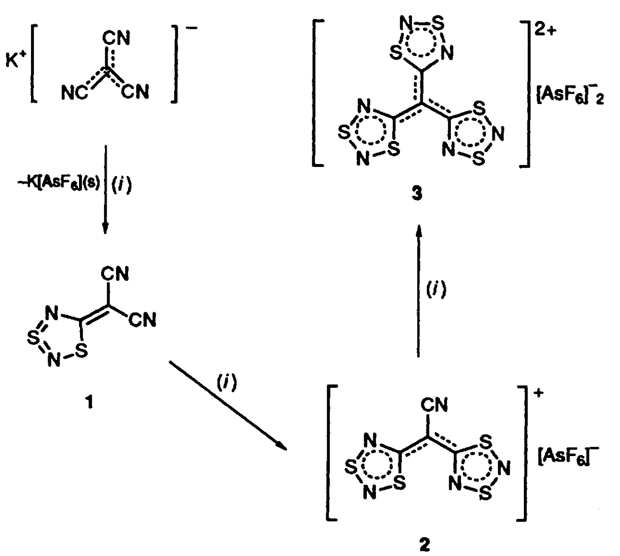
† *Supplementary data available* (No. SUP 56865, 3 pp): X-ray powder diffraction data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx xxv.

Non-SI unit employed: eV ≈ 1.60 × 10^{-19} J.



Scheme 2 Reactions of $[SNS][AsF_6]$ with $K[C(CN)_3]$. (*i*) $[SNS][AsF_6]$, SO_2

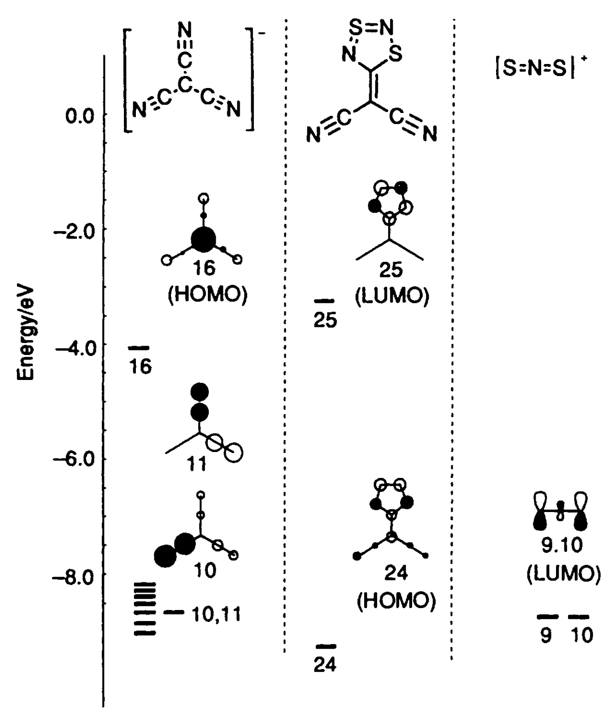


Fig. 1 Frontier molecular orbitals for $[C(CN)_3]^-$, **1** and $[SNS]^+$

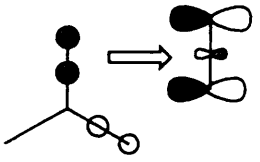
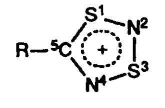


Fig. 2 Charge transfer from a filled $[C(CN)_3]^-$ orbital into the $[SNS]^+$ LUMO leading to cyclisation

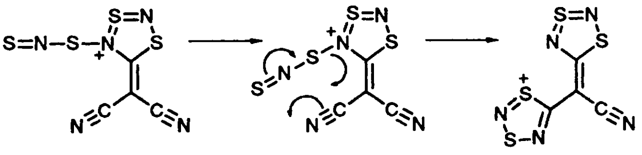
Molecular Orbital Calculations.—Calculations (at the PM3 level)[12,13] were carried out on tricyanomethanide and on its products with $[SNS][AsF_6]$. They indicated a somewhat more complex reaction mechanism than that initially anticipated.

The $[SNS]^+$ cation has previously been shown to undergo reactions *via* a symmetry-allowed [4 + 2] π cycloaddition process,[1–3] involving donation of electrons from the highest occupied molecular orbital (HOMO) of the dienophile to the $[SNS]^+$ lowest unoccupied molecular orbital (LUMO). However reaction of tricyanomethanide, itself, with $[SNS]^+$ does not appear to proceed through this HOMO–LUMO cycloaddition process, since the HOMO of $[C(CN)_3]^-$ does not retain the correct orbital symmetry to interact with the $[SNS]^+$ LUMO (see Fig. 1). Instead the reaction would appear (as shown in Fig. 2) to be electrostatically induced through $[SNS]^+/[C(CN)_3]^-$ attraction, followed by an electron-donation process from lower-lying filled MOs (10 and/or 11, −8.66 and −8.65 eV respectively), of the correct symmetry, into the $[SNS]^+$ LUMO (−8.42 eV).

A second cycloaddition process, between the first product, $(NC)_2C\overline{CNSNS}$, and $[SNS]^+$, would also appear to be hindered, on symmetry and energetic grounds, from undergoing a conventional [4 + 2] cycloaddition. However, Passmore and co-workers[4c] have recently proposed, for a similar reaction ($NC\overline{CNSNS}^+$ with $[SNS]^+$), that a second cycloaddition reaction may be induced by the approach of $[SNS]^+$ on the electronegative ring nitrogen (N^4) allowing a further cyclisation through a second molecular orbital, of similar energy to the HOMO, on the dieneophile. This is an in-plane π MO which is almost entirely located on the cyano group.



In the case of $(NC)_2C{=}\overline{CNSNS}$, there is, indeed, a lower-lying orbital with strong in-plane CN characteristics (19) but this appears some 3.5 eV lower in energy than the HOMO. We thus propose, on the basis of our MO calculations, an intermediate complex, $(NC)_2C{=}\overline{CNSNS}{-}SNS^+$ (see Fig. 3), in which the $[SNS]^+$ cation is bonded to the ring nitrogen (N^4, see above). The MO diagram of this complex shows a HOMO with strong contributions on both the CN and SNS functionalities, allowing in-plane cyclisation to $[(NC)C(\overline{CNSNS})_2]^+$ as shown below.



In the final stage of the reaction, *i.e.* the formation of the 3:1 product, we again see an intermediate $[SNS]^+$ complex undergoing intramolecular cyclisation to give the dication of salt **3**.

An important consequences of this mode of attachment of $[SNS]^+$ to the ring nitrogen is the stereochemical specificity induced in the final product(s). Owing to the formation of these complex intermediates, attack of the $[SNS]^+$ cation occurs only on one face of the cyano functionality (*i.e.* the face on the same side as the $\overline{CNSNS}$ ring nitrogen, N^4, with which the $[SNS]^+$ unit is interacting) and hence leads to only one product.* This specificity is seen in all bis- and tris-1,3,2,4-dithiadiazole/yliums so far examined,[4a,c] *viz.* $[C(\overline{CNSNS})_3]^{2+}$, $[\overline{SNSNC}{-}\overline{CNSNS}]^{2+}$ and p-$C_6H_4(\overline{CNSNS})_2$.

Structures.—The structures of compounds **1** and **3** were determined by single-crystal X-ray diffraction. Refined coordinates are given in Table 1 for **1** and in Table 2 for **3**. There are two independent neutral molecules of **1** in the crystallographic asymmetric unit (Fig. 4) and each is essentially planar (root-mean-square deviations from mean planes 0.039 and 0.042 Å). In-plane intermolecular CN ··· S interactions link the molecules together into planar sheets [Fig. 5; S(1) ··· N(7)

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* No evidence for the other stereoisomer of **3** was observed from powder diffraction studies (see SUP 56865).

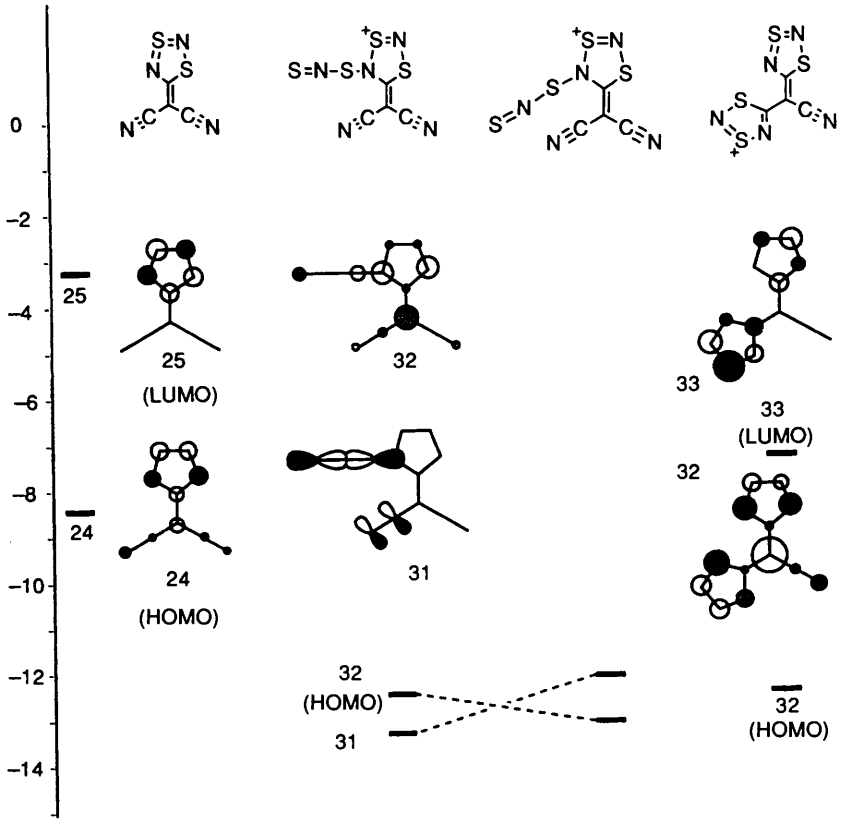


Fig. 3 Frontier molecular orbitals of compounds **1** and **2** and the proposed intermediate complex $[(CN)_2C(CNSNS)\text{–}SNS]^+$

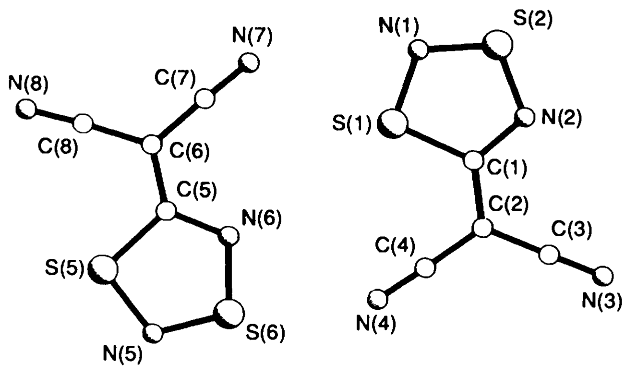
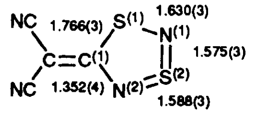


Fig. 4 The two independent molecules of **1**, showing the atom numbering scheme

3.103, S(5) ··· N(3′) 3.103, S(2′) ··· N(8) 3.051, S(6) ··· N(4) 2.971 Å, the prime denoting an atom in a symmetry-related molecule]; the dihedral angle between the mean planes of two adjacent molecules is 2.9°. These sheets are also linked to each other by further CN ··· S out-of-plane intermolecular interactions to give a three-dimensional network [Fig. 5; S(2) ··· N(3′) 3.163, S(6) ··· N(7′) 3.127 Å]; the dihedral angle between molecular planes is 117.3°. Each molecule thus engages in six CN ··· S secondary interactions involving its two dithiadiazole sulfur atoms and both nitrile nitrogen atoms, whilst the dithiadiazole nitrogen atoms are not involved.

The carbon–carbon double bond length in compound **1** compares well with that[14] in $MeS(Me_2N)C{=}C(CN)_2$, **4** (see Table 5), but it is longer than that observed in cubic tetracyanoethylene (tcne).[15] The CN bond lengths in **1** are also similar to those in **4** (1.148 and 1.154, compared with 1.130 and 1.132 Å, respectively) but shorter than those in cubic tcne. The average dithiadiazole bond lengths in **1** correspond better to those in NSNSC=O[16] than to those in $p\text{-}C_6H_4(CNSNS)_2$.[4a] This is probably due to a combination of (*i*) the greater exocyclic double-bond character in **1** (see below) and in O=CNSNS, and (*ii*) the electron-withdrawing effect of the dicyanomethyne group (*cf.* O=CNSNS) which is greater than that of 1,4-phenylene(dithiadiazole), $p\text{-}C_6H_4(CNSNS)_2$.



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The dication of **3** is essentially planar with C_{3h} symmetry (Fig. 6), the $[SNS]^+$ cations being added in a *cis* fashion as described above for **2**. Root-mean-square deviations for the three CNSNS rings are 0.005, 0.008 and 0.011 Å, and for the central C_4 unit 0.005 Å; the three rings have dihedral angles of 1.3, 5.6 and 2.2° to the C_4 mean plane. All three rings are thus chemically equivalent, with no significant differences in their geometries. There are, however, small differences among the three C–C bonds, but these minor distortions of the cation from ideal C_{3h} symmetry may be due to weak interactions with the anions and solvent molecules in the structure. In the crystal, anions and solvent molecules lie above and below each of the rings of the cations, and there are numerous S ··· F and S ··· O contacts between 2.90 and 3.25 Å involving the dithiadiazole sulfur atoms.

The bond lengths in the CNSNS rings of the dication of **3** compare well with other dithiadiazoliums (*e.g.* phenyl, methyl; see Table 6). As expected PM3 calculations on the parent dication indicate an even distribution of charge around the three CNSNS heterocyclic rings (each +0.73) which is also in accord with their equivalent geometries.

Reduction of dithiadiazolium cations has been shown[1a] to

Table 1 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
S(1)	2135.9(7)	1784.1(7)	1602.2(10)
S(2)	−7.2(7)	2572.5(6)	474.9(10)
S(5)	7507.7(7)	446.8(6)	5477.6(10)
S(6)	5867.6(7)	−340.3(7)	2938.9(10)
N(1)	1230(2)	2662(2)	1796(3)
N(2)	80(2)	1604(2)	−585(3)
C(1)	1147(2)	1151(2)	−56(3)
C(2)	1447(2)	273(2)	−721(3)
C(3)	621(3)	−201(2)	−2069(4)
N(3)	−61(2)	−583(2)	−3141(3)
C(4)	2556(3)	−173(2)	−7(4)
N(4)	3468(3)	−517(2)	619(4)
N(5)	7158(2)	−455(2)	4107(3)
N(6)	5366(2)	646(2)	3553(3)
C(5)	6154(2)	1097(2)	4822(4)
C(6)	5956(2)	1994(2)	5532(4)
C(7)	4858(3)	2502(2)	4939(4)
N(7)	3963(2)	2894(2)	4426(4)
C(8)	6882(3)	2436(2)	6785(4)
N(8)	7666(3)	2764(2)	7777(4)

Table 2 Atomic coordinates (× 10^4) for compound **3**

Atom	*x*	*y*	*z*
S(11)	3728.6(18)	4204.2(9)	4378.4(8)
S(12)	4277.6(21)	2783.0(9)	3996.4(9)
S(21)	3051.1(19)	3249.4(8)	1223.3(9)
S(22)	2397.2(19)	4246.8(9)	−168.6(9)
S(31)	2046.2(19)	5891.5(8)	1712.2(9)
S(32)	2217.0(19)	6349.7(9)	3451.8(10)
As(1)	2752.8(8)	4004.3(4)	7135.3(4)
As(2)	2110.8(8)	6421.0(4)	8965.7(4)
C(1)	3459(6)	3973(3)	3204(3)
N(11)	4252(6)	3378(3)	4765(3)
N(12)	3730(5)	3254(2)	3054(2)
C(2)	2809(5)	4190(3)	1518(3)
N(21)	2710(5)	3400(3)	109(3)
N(22)	2488(5)	4653(2)	804(2)
C(3)	2618(5)	5216(3)	2593(3)
N(31)	1847(5)	6587(2)	2394(3)
N(32)	2719(5)	5488(3)	3442(3)
C(4)	2972(6)	4474(3)	2443(3)
F(11)	3960(4)	4490(2)	8031(2)
F(12)	1101(4)	4584(2)	7113(2)
F(13)	2035(4)	3444(2)	7911(2)
F(14)	4374(4)	3388(2)	7165(2)
F(15)	3499(4)	4557(2)	6376(2)
F(16)	1557(4)	3511(2)	6240(2)
F(21)	915(5)	5632(3)	8759(4)
F(22)	3657(5)	5913(2)	9633(3)
F(23)	2997(5)	6232(3)	8059(3)
F(24)	585(4)	6924(3)	8288(3)
F(25)	1201(6)	6583(4)	9844(3)
F(26)	3345(5)	7186(2)	9195(3)
S(4)	998(5)	8636(3)	1046(2)
O(41)	2323(6)	8671(4)	693(4)
O(42)	−266(8)	8239(5)	1038(4)

Table 3 Bond lengths (Å) and angles (°) for compound **1**

S(1)–N(1)	1.624(3)	S(1)–C(1)	1.765(3)
N(1)–S(2)	1.576(3)	S(2)–N(2)	1.589(3)
N(2)–C(1)	1.356(4)	C(1)–C(2)	1.385(4)
C(2)–C(3)	1.423(4)	C(2)–C(4)	1.411(4)
C(3)–N(3)	1.148(4)	C(4)–N(4)	1.154(4)
S(5)–N(5)	1.637(3)	S(5)–C(5)	1.767(3)
N(5)–S(6)	1.575(3)	S(6)–N(6)	1.586(3)
N(6)–C(5)	1.347(4)	C(5)–C(6)	1.384(4)
C(6)–C(7)	1.424(4)	C(6)–C(8)	1.419(4)
C(7)–N(7)	1.151(4)	C(8)–N(8)	1.146(4)
N(1)–S(1)–C(1)	96.5(1)	S(1)–N(1)–S(2)	112.5(2)
N(1)–S(2)–N(2)	105.3(1)	S(2)–N(2)–C(1)	112.1(2)
S(1)–C(1)–N(2)	113.4(2)	S(1)–C(1)–C(2)	122.3(2)
N(2)–C(1)–C(2)	124.3(2)	C(1)–C(2)–C(3)	120.0(3)
C(1)–C(2)–C(4)	119.7(2)	C(3)–C(2)–C(4)	120.2(3)
C(2)–C(3)–N(3)	178.8(4)	C(2)–C(4)–N(4)	177.8(4)
N(5)–S(5)–C(5)	96.4(1)	S(5)–N(5)–S(6)	112.3(2)
N(5)–S(6)–N(6)	105.2(1)	S(6)–N(6)–C(5)	112.9(2)
S(5)–C(5)–N(6)	113.3(2)	S(5)–C(5)–C(6)	122.4(2)
N(6)–C(5)–C(6)	124.3(3)	C(5)–C(6)–C(7)	120.4(2)
C(5)–C(6)–C(8)	119.3(3)	C(7)–C(6)–C(8)	120.2(3)
C(6)–C(7)–N(7)	178.1(3)	C(6)–C(8)–N(8)	176.9(4)

Table 4 Bond lengths (Å) and angles (°) for the cation of compound **3**

C(1)–S(11)	1.745(5)	C(1)–N(12)	1.329(7)
C(1)–C(4)	1.418(7)	S(11)–N(11)	1.602(5)
N(11)–S(12)	1.557(5)	S(12)–N(12)	1.599(4)
C(2)–S(21)	1.756(6)	C(2)–N(22)	1.316(6)
C(2)–C(4)	1.433(7)	S(21)–N(21)	1.626(4)
N(21)–S(22)	1.571(5)	S(22)–N(22)	1.594(4)
C(3)–S(31)	1.755(5)	C(3)–N(32)	1.328(6)
C(3)–C(4)	1.384(8)	S(31)–N(31)	1.629(5)
N(31)–S(32)	1.578(5)	S(32)–N(32)	1.592(5)
S(11)–C(1)–N(12)	113.9(3)	S(11)–C(1)–C(4)	125.9(4)
N(12)–C(1)–C(4)	120.2(4)	C(1)–S(11)–N(11)	95.7(2)
S(11)–N(11)–S(12)	114.5(3)	N(11)–S(12)–N(12)	103.1(2)
C(1)–N(12)–S(12)	112.7(3)	S(21)–C(2)–N(22)	114.5(4)
S(21)–C(2)–C(4)	125.6(4)	N(22)–C(2)–C(4)	119.9(5)
C(2)–S(21)–N(21)	95.1(2)	S(21)–N(21)–S(22)	113.7(3)
N(21)–S(22)–N(22)	103.4(2)	C(2)–N(22)–S(22)	113.2(4)
S(31)–C(3)–N(32)	113.4(4)	S(31)–C(3)–C(4)	124.7(4)
N(32)–C(3)–C(4)	121.9(5)	C(3)–S(31)–N(31)	96.5(2)
S(31)–N(31)–S(32)	112.5(3)	N(31)–S(32)–N(32)	104.0(2)
C(3)–N(32)–S(32)	113.6(4)	C(1)–C(4)–C(2)	118.7(5)
C(1)–C(4)–C(3)	120.5(4)	C(2)–C(4)–C(3)	120.8(4)

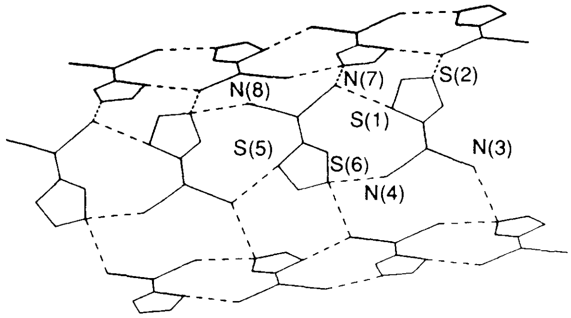

Fig. 5 Intermolecular interactions within and between sheets of molecules in the structure of compound **1**. The view direction is the same as for Fig. 4

yield the corresponding dithiadiazole neutral free-radical species; in the case of the 1,3,2,4-dithiadiazoles these have been found to be photochemically unstable with respect to rearrangement to their 1,2,3,5-dithiadiazole analogues.[3b] (The rearrangement process takes between a few minutes and several weeks, depending upon the organic substituent.)

Cyclic Voltammetry.—Earlier cyclic voltammetric studies[4a,18] on a variety of dithiadiazolium cations have shown that they can be reduced readily to their neutral free-radical analogues and, in some cases, the reduction to the dithiadiazolide anion is partially reversible (the reversibility is dependent upon the sweep rate).

Cyclic voltammetry on $(\mathrm{NC})_2\mathrm{C}\overline{\mathrm{CNSNS}}$ **1**, [Fig. 7(*a*)] showed that it may be reduced ($E_{\mathrm{p}/2} = -0.41$ V) to the radical anion (peak 1) in acetonitrile and that this process is reversible. Compound **2**, $[(\mathrm{NC})\mathrm{C}(\overline{\mathrm{CNSNS}})_2][\mathrm{AsF}_6]$, is less readily

Table 5 Selected bond lengths (Å) in compound **1** and comparable systems

	p-C$_6$H$_4$(CNSNS)$_2$	(NC)$_2$CC=CNSNS **1**		NSNSC=O
C(1)–N(2)	1.276(4)	1.356(4)	1.347(4)	1.374(7)
N(2)–S(2)	1.646(4)	1.589(3)	1.586(3)	1.584(4)
S(2)–N(1)	1.695(4)	1.576(3)	1.575(3)	1.572(5)
N(1)–S(1)	1.632(4)	1.624(3)	1.637(3)	1.630(4)
S(1)–C(1)	1.775(4)	1.765(3)	1.767(3)	1.813(5)
Ref.	4*a*	This work		16

	(NC)$_2$C=CNSNS **1**	tcne (cubic)	MeS(Me$_2$N)C=C(CN)$_2$	(Me$_2$N)$_2$C=C(CN)$_2$
C=C	1.385(4)	1.353(3)	1.397(8)	1.407(4)
	1.384(4)			
C–C=C	1.411(4)	1.432(2)	1.430(8)	1.410(5)
	1.423(4)			
	1.424(4)			
	1.419(4)			
C≡N	1.148(4)	1.166(2)	1.130(9)	1.143(5)
	1.154(4)		1.132(10)	1.151(6)
	1.151(4)			
	1.146(4)			
Ref.	This work	15	14	14

Table 6 Selected bond lengths (Å) in compound **3** and comparable systems

			C(CNSNS)$_3{}^{2+}$		
	PhCNSNS$^+$	MeCNSNS$^+$	C(1) ring	C(2) ring	C(3) ring
N(2)–S(2)	1.576(7)	1.57(2)	1.599(4)	1.594(4)	1.592(5)
S(2)–N(1)	1.561(8)	1.59(2)	1.557(5)	1.571(5)	1.578(5)
N(1)–S(1)	1.596(8)	1.63(2)	1.602(5)	1.626(4)	1.629(5)
S(1)–C(1)	1.732(8)	1.77(2)	1.745(5)	1.756(6)	1.755(5)
C(1)–N(2)	1.336(9)	1.32(3)	1.329(7)	1.316(6)	1.328(6)
Ref.	17	3*a*	This work		

reduced to the corresponding anion ($E_{p/2} = -0.525$ V) or to the dianion ($E_{p/2} = -0.675$ V) [Fig. 7(*b*) peaks 2 and 3], but it rapidly and reversibly accepted one electron to form the neutral species (peak 1). Compound **3**, [C(CNSNS)$_3$][AsF$_6$]$_2$, was more readily reduced than either **2** or **3**, [Fig. 7(*c*)] to the monocation ($E_{p/2} = 0.03$ V) and further to the neutral species ($E_{p/2} = -0.1$ V) (both peaks 1 and 2 were reversible).

Metathesis of compound **3** with 2 equivalents of tetrabutylammonium chloride yielded the corresponding dichloride, [C(CNSNS)$_3$]Cl$_2$. Reduction of this salt with SbPh$_3$ gave the associated 1,3,2,4-dithiadiazole radical cation and neutral diradical (observed by ESR spectroscopy). As a continuation of this work, we are presently studying the redox chemistry of these systems.[19]

Conclusion

The reactions of [SNS][AsF$_6$] with K[C(CN)$_3$] have provided the first example, to our knowledge, of [SNS]$^+$ reacting with an anion containing an unsaturated centre. These cycloaddition processes do not appear to proceed through conventional frontier-orbital HOMO–LUMO interactions. Possible reaction pathways have been examined by PM3 molecular orbital calculations and the geometries of the reaction products have been rationalised. The product of the 1:1 reaction between [C(CN)$_3$]$^-$ and [SNS]$^+$, (NC)$_2$CCNSNS **1**, shows the tendency of these 1,3,2,4-dithiadiazoles to form polymeric rather than the dimeric solid-state structures favoured by the 1,2,3,5-dithiadiazoles. Reactions of 2 or 3 equivalents of [SNS][AsF$_6$] with K[C(CN)$_3$] led to the mono- and bis-dithiadiazolium salts (**2** and **3**, see Scheme 1); the latter species possesses C_{3h} symmetry.

Experimental

General Procedures.—All reactions and manipulations were carried out under an atmosphere of dry nitrogen (the latter employing a Vacuum Atmospheres Corporation HE 43-2 glove-box and HE 493 dri-train). Solvents were distilled, dried and degassed before use. The IR spectra were recorded as Nujol mulls between KBr plates using a Perkin-Elmer 577 grating spectrophotometer, mass spectra on a VG Analytical 7070E spectrometer, ESR spectra on a Varian V4502 spectrometer and ^{13}C and ^{14}N NMR spectra on a Brücker AMX 500 spectrometer. The C, H and N analyses were carried out using a Carlo-Erba 1106 elemental analyser.

Cyclic voltammograms were recorded, using a Ag–Ag$^+$ reference electrode[20] [calibrated with reference to the saturated calomel electrode (SCE)], a potential-wave generator (type CV-1B; Bioanalytical Systems, W. Lafayette, IN) and a Linseis x-y chart recorder (type LY 17100). Solutions (*ca.* 1 × 10^{-3} mol dm^{-3}) of the electroactive species were prepared in MeCN and 0.1 mol dm^{-3} NBu$_4$BF$_4$ was used as supporting electrolyte.

Starting Materials.—Dithionitryl hexafluoroarsenate(v) was prepared by an amended literature route[21] (washing the crude material with CH$_2$Cl$_2$ improves the yield by 20%): S$_4$N$_4$ (1.1 g) and S (0.74 g) were placed in one leg of a two-limbed reaction vessel. Sulfur dioxide (*ca.* 10 cm^3) and a trace of Br$_2$ were condensed in before the addition of AsF$_5$ (6 g). The system was allowed to warm to room temperature and then stirred for 12 h. The solvent was removed and the crude olive-green product stirred in CH$_2$Cl$_2$ for 24 h to yield yellow [SNS][AsF$_6$] under a red solution. The impurities were filtered off and the product washed briefly with further CH$_2$Cl$_2$ by back-condensation. Recovered yield of [SNS][AsF$_6$]: 5.80 g (95%).

Potassium tricyanomethanide (Strem) was used after

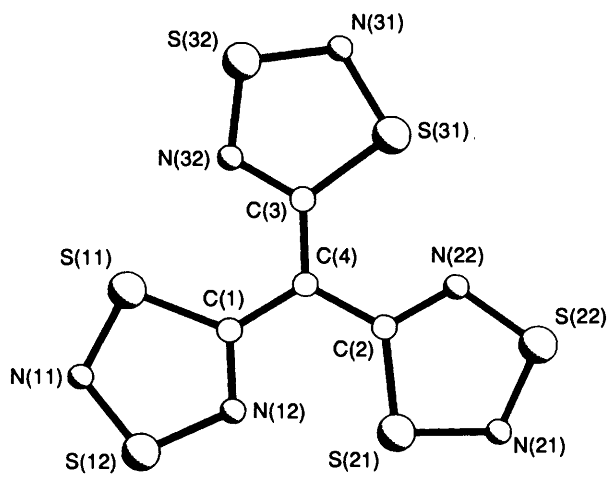

Fig. 6 The dication of compound **3**, showing the atom numbering scheme

washing with thf, $[\mathrm{NBu^n}_4]\mathrm{Cl}$ was precipitated twice from acetone by addition of diethyl ether and baked at 75 °C for 6 h *in vacuo* and $\mathrm{SbPh_3}$ (Aldrich) was used without further purification.

Preparations.—$(\mathrm{NC})_2\mathrm{C}(\overline{\mathrm{CNSNS}})$ **1**. Potassium tricyanomethanide (218 mg, 1.7 mmol) was stirred with a slight excess of $[\mathrm{SNS}][\mathrm{AsF_6}]$ (450 mg, 1.7 mmol) in liquid $\mathrm{SO_2}$ in a two-limbed reaction vessel for 1.5 h to yield a deep purple-black solid under a dichroic red-purple solution. Filtration and repeated back-extraction gave a deep purple-black solid upon solvent removal from the filtrate. Extraction with $\mathrm{CH_2Cl_2}$ for 2 d in a closed extractor[22] followed by solvent removal gave a purple filtrate (205 mg, 72%) and brown residue. IR $\nu_{max}(\mathrm{cm^{-1}})$: 422(sh), 635w, 656w, 692vw, 722m, 750(sh), 758s, 760m, 935(sh), 940m, 953m, 966m, 1020w, 1150vw, 1205s, 1275w, 1305w, 2210s and 2225s. Mass spectroscopy (electron impact): m/z 246 (51.77), 160 (100), 78 (100) and 46 (15.79). ^{14}N NMR: δ −29.2, −88.3 and −112.9 (1:1:2). ^{13}C NMR: only CN seen at δ 126.1. UV/VIS: 248 (65), 251 (65), 330 (63), 418 (9), 556 (100) and 577 nm (100% relative intensity).

In order to obtain single crystals of compound **1** for X-ray crystallography, a sample was sublimed at 10^{-7} Torr (*ca.* 1.33×10^{-5} Pa) and 85 °C for 5 d and the small, black, lustrous prisms collected at a constriction in the sublimer. This material analysed well (Found: C, 28.25; N, 33.30. Calc.: C, 28.55; N, 33.30%).

$[(\mathrm{NC})\mathrm{C}(\overline{\mathrm{CNSNS}})_2][\mathrm{AsF_6}]$ **2**. Potassium tricyanomethanide (59 mg, 0.46 mmol) was stirred with a slight excess of $[\mathrm{SNS}][\mathrm{AsF_6}]$ (247 mg, 0.92 mmol) in liquid $\mathrm{SO_2}$ in a two-limbed reaction vessel for 16 h to yield a deep red-purple solution. Filtration and repeated back extraction with $\mathrm{SO_2}$ followed by continuous extraction of the filtrate with $\mathrm{CH_2Cl_2}$ in a closed extractor for 16 h yielded a residual reddish brown solid (120 mg, 59% recovered yield). The IR spectrum of this material suggested that the expected product had been formed; elemental analysis was in agreement with the expected C:N ratio for compound **2** but volatile $\mathrm{SO_2}$ of solvation caused inconsistent absolute values of analyses. IR $\nu_{max}(\mathrm{cm^{-1}})$: 400s, 440m, 455w, 588w, 638m, 650m, 668m, 698s (br), 720(sh), 780m, 798m, 904m, 930m(br), 960(sh), 965m, 980m, 1017w, 1034w, 1160w (br), 1225m, 1237(sh), 1275(sh), 1280m, 1310m, 1350(sh), 1370 (sh), 1415s and 2220m.

$[\mathrm{C}(\overline{\mathrm{CNSNS}})_3][\mathrm{AsF_6}]_2\cdot\mathrm{SO_2}$ **3**. Potassium tricyanomethanide (130 mg, 1 mmol) was stirred with a slight excess of $[\mathrm{SNS}][\mathrm{AsF_6}]$ (820 mg, 3 mmol) in liquid $\mathrm{SO_2}$ in a two-limbed reaction vessel for 16 h to yield a deep orange-red solid under a red solution. Filtration and repeated back-extraction gave a red solid and solution (from filtrate), and a residual heterogeneous, brown-pink solid (shown by IR spectroscopy to be $\mathrm{K}[\mathrm{AsF_6}]$). Solvent removal yielded a crude red solid which was extracted with $\mathrm{CH_2Cl_2}$ in a closed extractor for 3 d (to remove impurities) before being recrystallised from liquid $\mathrm{SO_2}$. Slow solvent removal yielded red crystals and a red microcrystalline powder (655 mg, 84%). Crystals suitable for X-ray analysis were picked from the solid mass. UV/VIS: 485 (90), 339 (100), 304 (74) and 242 nm (96% relative intensity). IR spectra showed no C≡N stretch (at 2200 $\mathrm{cm^{-1}}$) and the presence of $\mathrm{AsF_6}^-$ (strong, broad bands at 398 and 692 $\mathrm{cm^{-1}}$) as well as $\mathrm{SO_2}$ of solvation (528 and 1150 $\mathrm{cm^{-1}}$); $\nu_{max}/\mathrm{cm^{-1}}$ 398vs, 452m, 528vw, 570w, 647m, 650(sh), 692s (br), 720(sh), 738m, 773w, 800m, 937m, 945(sh), 974m, 980(sh), 1030w, 1090w, 1150w, 1265m, 1310w, 1335m, 1440(sh),

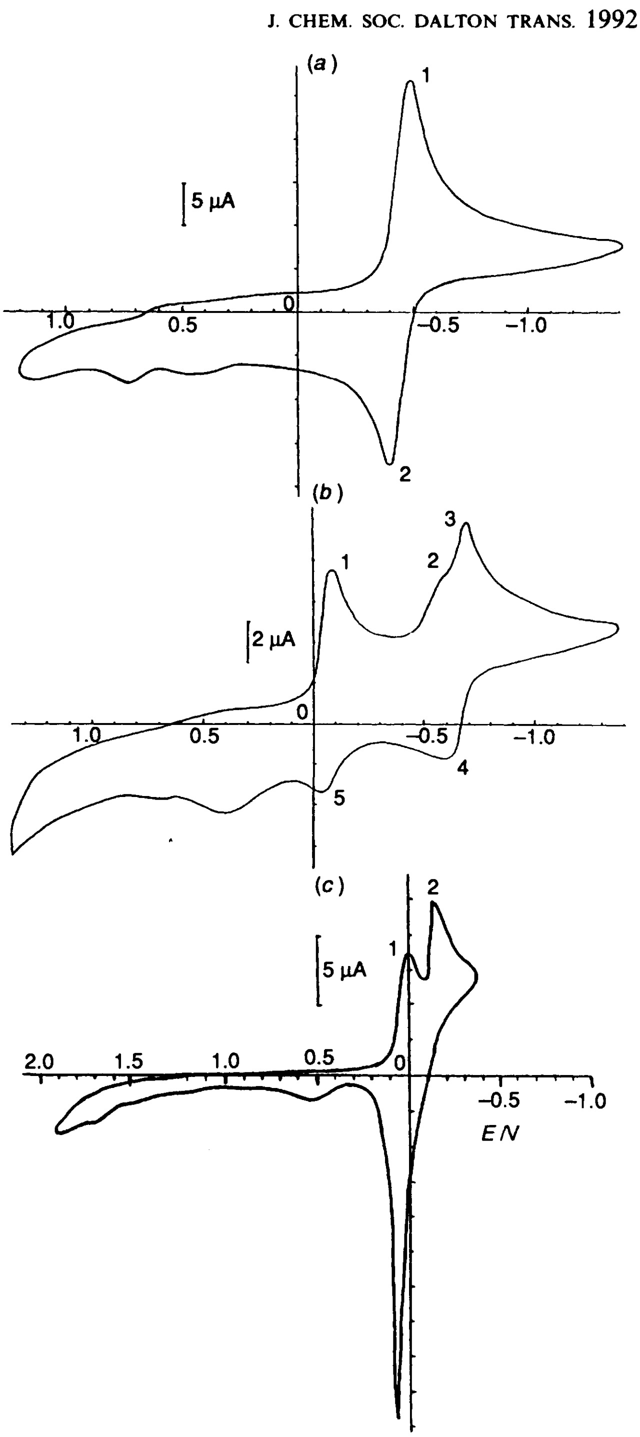

Fig. 7 Cyclic voltammograms of compounds **1**(*a*), **2**(*b*) and **3**(*c*)

1500m, Elemental analysis was, again, in agreement with the expected C:N ratio for compound **3**, but inconsistent results were obtained (due to volatile SO_2 of crystallisation being present).

$[\mathrm{C}(\overline{\mathrm{CNSNS}})_3]\mathrm{Cl}_2$. Tetrabutylammonium chloride (420 mg, 1.4 mmol) was stirred with $[\mathrm{C}(\overline{\mathrm{CNSNS}})_3][\mathrm{AsF}_6]_2$ (500 mg, 0.7 mmol) in acetonitrile in a two-limbed reaction vessel for 1 h to yield a brick-red precipitate under a purple-red liquor. Filtration and repeated back-extraction followed by solvent removal gave a brownish white crystalline residue and a pale brick-red solid which was washed for 16 h in a closed extractor with acetonitrile. The residual, highly air- and moisture-sensitive, brick-red solid (200 mg, 73%) analysed well as the dichloride (Found: C, 13.20; H, 0.55; N, 21.35. Calc.: C, 12.55; N, 21.25%). IR showed no $[\mathrm{AsF}_6]^-$ to be present, $\nu_{max}/\mathrm{cm}^{-1}$: 438m, 565w, 590vw, 642m, 685vw, 725m, 790m, 845w, 917m (br), 968s (br), 1020m, 1110m (br), 1260m, 1292m and 1430(sh).

Reductions of $[\mathrm{C}(\overline{\mathrm{CNSNS}})_3]\mathrm{Cl}_2$.—ESR spectra of *in situ* reductions of the dichloride with $SbPh_3$ revealed a 1:1:1 triplet indicative of the 1,3 radical.

X-Ray Crystallography.—Crystal data for compound **1**. $C_4N_4S_2$, M_r = 168.19, monoclinic, space group $P2_1/c$, a = 11.8595(10), b = 13.2788(10), c = 8.4688(6) Å, β = 106.558(5)°, U = 1278.4 Å^3, Z = 8, D_c = 1.748 g cm^{-3}, λ-(Mo-Kα) = 0.710 73 Å, μ = 0.71 mm^{-1}, $F(000)$ = 672.

Data collection and processing. A crystal of size 0.16 × 0.20 × 0.52 mm, sealed in a capillary tube, was examined on a Stoe-Siemens diffractometer equipped with a Cryostream cooler;[23] all measurements were made at 240 K. Cell parameters were refined from 2θ values (20–25°) of 32 reflections measured at ±ω. Data collection employed ω–θ scans and on-line profile fitting:[24] $2\theta_{max}$ = 50°, index ranges h 0–14, k 0–15, l −10 to 10. No significant variation was observed for three standard reflections monitored at intervals. 2252 Unique reflections were measured, of which 1555 had $F > 4\sigma_c(F)$ (σ_c from counting statistics only). No absorption or extinction corrections were applied.

Structure determination.[25] Atoms were located from Patterson and difference syntheses, and refined with anisotropic thermal parameters to minimise $\Sigma w\Delta^2$, with $\Delta = |F_o| - |F_c|$ and $w^{-1} = \sigma^2(F) = \sigma_c^2(F) - 1 + 36G - 19G^2 + H - 38GH$ ($G = F_o/F_{max}$, $H = \sin\theta/\sin\theta_{max}$).[26] Atomic scattering factors were taken from ref. 27. At convergence, R = 0.0321, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$ = 0.0409, goodness of fit = 1.11 for 181 parameters; maximum shift/e.s.d. = 0.001. All features in a final difference synthesis lay between +0.28 and −0.24 e Å^{-3}.

Crystal data for compound **3**. $C_4As_2F_{12}N_2O_2S_7$, M_r = 766.3, monoclinic, space group $P2_1/c$, a = 8.168(3), b = 17.839(6), c = 14.747(5) Å, β = 103.12(3)°, U = 2092.7 Å^3, Z = 4, D_c = 2.432 g cm^{-3}, μ(Mo-Kα) = 3.98 mm^{-1}, $F(000)$ = 1472.

Data collection and processing. As for compound **1**, except: crystal size 0.25 × 0.30 × 0.80 mm; index ranges h −9 to 9, k 0–21, l 0–17, together with a partial set of equivalent reflections; semiempirical absorption corrections, with transmission factors 0.09–0.11; 6078 reflections measured, 3705 unique, 2892 with $F > 4\sigma_c(F)$, R_{int} = 0.025 for merging of equivalent reflections.

Structure determination. As for compound **1**, except: $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 226 - 2906G + 5755G^2 - 386H + 160H^2 + 2813GH$; isotropic extinction parameter x = 5.8(8) × 10^{-7}, whereby $F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{\frac{1}{4}}$; R = 0.0550, R' = 0.0318, goodness of fit = 1.64 for 299 parameters, maximum shift/e.s.d. = 0.17, extremes of final difference synthesis +1.29 and −1.13 e Å^{-3}, close to the solvent molecule, which shows high thermal motion and may be affected by disorder.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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