

The High Yield Preparation, Characterisation, and Gas Phase Structure of the Thermally Stable $\text{CF}_3\text{CSN}\text{SCCF}_3$, 4,5-Bis(trifluoromethyl)-1,3,2-dithiazolyl and the X-Ray Crystal Structure of Benzo-1,3,2-dithiazolyl

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The very thermally stable, but photochemically sensitive radical, 4,5-bis(trifluoromethyl)-1,3,2-dithiazolyl has been prepared, isolated, and fully characterised including a gas phase structure, and found to be paramagnetic in the liquid state at room temperature; the X-ray structure of benzo-1,3,2-dithiazolyl has been obtained for comparison.

There are few examples of stable neutral† free radical compounds of the main group elements that do not owe their monomeric paramagnetic nature to effective steric hindrance or extensive electron delocalisation [as in *e.g.* diphenylpicrylhydrazyl (DPPH) and $(\text{C}_6\text{Cl}_5)_3\text{C}\cdot$].^{2,3} Molecular oxygen and ClO_2 are examples that are paramagnetic in all phases.⁴ In

† There are more examples of salts containing paramagnetic ions of the main group elements *e.g.* O_3^- , O_2^+ , O_2^- , I_2^+ , Br_2^+ .¹

addition, certain nitroxides form an exclusive class of compounds which are essentially paramagnetic in the liquid state, but are diamagnetic as solids.^{5,6} We report the new high yield preparation and isolation of a very thermally stable, non-sterically hindered, C-S-N containing, heterocyclic radical (**1**), which is a paramagnetic liquid at room temperature and can be classified with $(\text{CF}_3)_2\text{NO}$.⁵ Compound (**1**) was first prepared in dilute solution by reaction of S_4N_2 with $\text{CF}_3\text{C}\equiv\text{CCF}_3$ and was identified by *e.s.r.* spectroscopy.⁷ It was noted to have unusual stability and to show no dimerisation at

low temperature. In the pure state we find (1) to be diamagnetic and likely dimeric in the solid state. Another known derivative (2; R = Me,^{8,9} R = H⁹) and derivatives of the related heterocycle (3; R = CF₃, Ph),¹⁰ are also diamagnetic solids at room temperature, and are dimeric. Despite its paramagnetic nature, (1) exhibits remarkable thermal stability [$<275^{\circ}\text{C}$, cf. (2; R = H) m.p. 85°C (decomp.)]. Therefore it may be described as a type of 'thermally inert free radical'³ and is the first example of an aliphatic derivative of a 7π -1,3,2-dithiazolyl ring obtained on a preparative scale. This unusual stability makes it an excellent candidate for further study, and like (CF₃)₂NO,⁵ it may have an extensive chemistry. It is also of interest as a precursor to charge transfer conducting salts⁹ and to C-S-N containing, thermally stable, conducting polymers.¹¹ We have begun by examining a number of physical properties of (1), presented below, including a gas phase structure of the free radical monomer. For comparison we have determined the X-ray crystal structure of compound (2; R = H) which is observed as dimeric units bound in a head-to-tail fashion by $\pi^*-\pi^*$, S-S interactions.

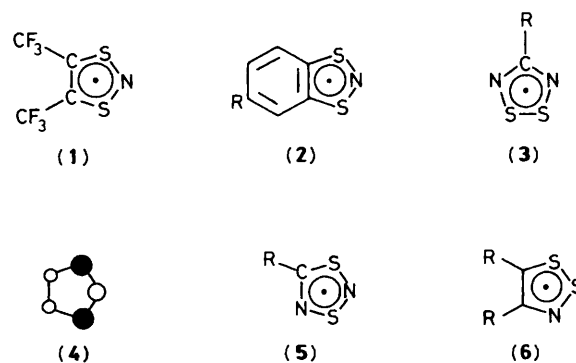
We have developed a high yield synthesis of (1) from the corresponding cation and have isolated and fully characterised (1) as an indefinitely thermally stable radical. In a typical reaction hexafluorobut-2-yne (1.30 g, 11.10 mmol) was reacted with dithionitronium hexafluoroarsenate (1.34 g, 5.01 mmol) in liquid SO₂ (4.33 g) for 4 hours and gave a quantitative yield of 4,5-bis(trifluoromethyl)-1,3,2-dithiazolium hexafluoroarsenate (2.03 g, 4.73 mmol, 95%) (cf. reactions of S₂N⁺ with triple bonds¹²). The white crystalline solid was fully characterised by i.r. and n.m.r. spectroscopy and elemental analysis. This cation (3.08 g, 7.18 mmol) was reduced by reaction with an excess of finely ground sodium dithionite (6.89 g, 39.59 mmol) in liquid SO₂ (14.43 g) overnight at room temperature. The volatile products in the resulting black solution were fractionally distilled through a series of U-tube traps at -15 , -80 , and -196°C under a dynamic vacuum. The black liquid collected at -15°C was purified by repeated fractional distillation to give pure 4,5-bis(trifluoromethyl)-1,3,2-dithiazolyl, (1) (1.54 g, 6.41 mmol, 88%) m.p. 12°C , v.p. 20 Torr at 25°C , as an air sensitive black-green liquid beneath a blue gas, $\Delta H_{\text{vap}} = 9.1(\pm 1)$ kcal mol⁻¹,[‡] b.p. (extrapolated) = $119(\pm 2)^{\circ}\text{C}$. Compound (1) has been characterised by i.r., mass ($m/z = 240$), u.v.-visible [λ_{max} (ε) in hexane: 287 (2260), 227 (2720), 560 (110), 738 nm (260)] and e.s.r.⁷ spectroscopy, elemental analysis, and magnetic susceptibility. Oxidation of (1) using a variety of oxidants (e.g. AsF₅, Cl₂, Br₂) gave a quantitative yield of the original cation. A sample of (1) in a sealed glass tube was heated to 260°C for 1 hour without any visual change but decomposed noticeably above 275°C . The yellow liquid formed upon decomposition was shown by ¹⁹F n.m.r. spectroscopy to be a mixture of compounds with the major component (ca. 60%) being CF₃CSSCCF₃.¹³ Similar decomposition products were observed when (1) was exposed to sunlight for 2 hours. This photolytic instability requires that (1) be stored in the dark.

The magnetic moment of (1) was measured by the Gouy method¹⁴ using Ni(en)₃S₂O₃ (en = ethylenediamine) as a standard, $\chi_{\text{g}} = 3.8 (\pm 0.4) \times 10^{-6}$ c.g.s. ($1.53 \mu_{\text{B}}$) at 20°C . However, a solid sample of (1) was found to be diamagnetic, $\chi_{\text{g}} = 0$ at 9°C . A comparative series of Gouy measurements on solutions of (1) in CFCl₃ (between 1.6 and 4.5 M) employing NiCl₂/H₂O solutions as a standard, gave $\chi_{\text{g}} = 5.8(\pm 0.6) \times$

10^{-6} c.g.s. ($1.91 \mu_{\text{B}}$) at 20°C as a maximum value by extrapolation. Assuming this corresponds to a fully dissociated sample of (1) and that the dimer is diamagnetic, then the observed magnetic susceptibility of the pure liquid is indicative of an equilibrium mixture consisting of ca. 65% free radical and ca. 35% diamagnetic dimer (Wiedemann additivity law¹⁵). Compound (2; R = H) is reported to be paramagnetic in the solid state. However we have found from Faraday¹⁴ magnetic susceptibility measurements that $\chi_{\text{g}} = 0.3(\pm 0.03) \times 10^{-6}$ c.g.s. ($0.58 \mu_{\text{B}}$ assuming the monomer is responsible for paramagnetism) which corresponds to less than 10% monomer in the bulk. This residual paramagnetism may be related to that observed for a variety of weakly bound dimer compounds and is not necessarily indicative of free monomers in the solid state.¹⁶

Quantitative e.s.r. studies on concentrated solutions of (1) (ca. 30% w/w) and (2; R = H) (dilute solution) in CFCl₃ at a range of temperatures ($T = 318$ – 188 K) showed no change in the concentration of radical with T , indicating that ΔH (dimerisation) (ΔH_{d}) for these compounds in CFCl₃ is very close to zero. This provides an interesting comparison with ΔH_{d} reported for (CF₃)₂NO in CFCl₃ to be -2.5 kcal mol⁻¹.¹⁷ Evidently ΔH_{d} for (1) and (2; R = H) are significantly lower than this and may be positive in solution. The ΔH_{d} value for a pure sample of (1) as a liquid, which we have estimated by means of variable temperature magnetic susceptibility measurements, is $-3.5(\pm 1.5)$ kcal mol⁻¹, hence its paramagnetic nature in the liquid state.¹⁸

The absolute structure of (1) has been determined in the gas phase by electron diffraction techniques.¶ A planar ring structure was confirmed, as illustrated in (1). The pertinent bond lengths and angles are listed in Table 1. While the bonds are comparable with those expected in the corresponding cation (cf. X-ray structure of derivative, R = Me, H, of the cation¹²), there are some interesting differences. The S-N (1.63 Å, cf. 1.59/1.62 Å) and C-S (1.75 Å, cf. 1.67/1.68 Å) bonds are both longer in the neutral radical, but the C-C (1.32 Å, cf. 1.40 Å) bond is significantly shorter than observed in



‡ Gouy measurements gave a slightly larger value $\chi_{\text{g}} = 2.3(\pm 0.2) \times 10^{-6}$ c.g.s. This may be due to the increase in surface area upon grinding of the sample, required in the Gouy method. A phase change is also possible, and both may lead to an increase in monomer concentration.

¶ The electron diffraction intensities were recorded at two camera distances (25 and 50 cm) with the Balzers Gas Diffractograph.¹⁹ The electron wavelength (about 60 kV accelerating voltage) was calibrated by ZnO diffraction patterns. The sample, stainless steel inlet system, and nozzle were at room temperature. The camera pressure during the experiment was approximately 5×10^{-6} Torr. Details of the data reduction procedure and structure analysis will be published in a later full paper.

‡ 1 cal = 4.184 J.

Table 1. Bond lengths and angles for the gas phase structure of $\text{CF}_3\text{CSNSCCF}_3$ (1).^a

Bond lengths (Å)		Bond angles (°)	
C-C	1.324(14)	C-C-S	114.8(6) ^b
C-S	1.749(5)	C-S-N	96.5(12) ^b
S-N	1.634(4)	S-N-S	117.3(9)
C-CF ₃	1.481(6)	C-C-CF ₃	127.3(5)
C-F	1.330(3)	F-C-F	107.4(3)

^a Error limits are 2σ values and include a possible scale error of 10%.

^b Dependent parameter.

the cation. Although the CF_3 substituents may be responsible, in part, for the short C-C bond, the nature of the π^* -SOMO (CNDO) (4) of this ring framework provides a simple rationale. Occupation of (4) in the neutral radical provides additional bonding between the carbon centres but results in antibonding interactions over the other bonds in the ring.

In order to understand the diamagnetic nature of (1) and (2; R = H) in the solid state, we have determined the X-ray crystal structure of (2; R = H).^{||} [Crystals of (1) obtained so far have been unsuitable for X-ray studies.] Compound (2; R = H) was prepared by the literature method⁹ and high quality, shiny, metallic, gold crystals were obtained by sublimation of the crystalline solid in an evacuated (*ca.* 10^{-3} Torr) sealed tube by heating to 80 °C over a period of 2 days, crystal growth occurring on the glass surface at room temperature. A PLUTO²¹ view of the dimer unit of (2; R = H) is shown in Figure 1 with the pertinent bond lengths and angles. The dimeric arrangement accounts for the diamagnetic behaviour of the material. While the bond lengths and angles within each ring compare very closely with those of the gas phase structure of the monomeric unit of (1), the gross features of the structure provide some very important information. The dimer interaction in a π^* - π^* fashion predominates at the sulphur centres, as observed for related dimers of the disulphide species (3),¹⁰ and as expected from the sulphur based SOMO (4). The S-S dimer bonds of (2; R = H) [3.174(9) Å] are significantly longer than those observed for the disulphide compounds (3) [mean: S-S = 3.109(5) Å in (3; R = Ph¹⁰)]. This may relate to the low ΔH_d observed for the S-N-S containing radicals, assuming a similar solid state structure for (1). A long contact is evident at each sulphur centre in (2; R = H) [S-S = 3.4771(8) Å] that could be responsible for the weaker π^* - π^* bond. However, a great number of contacts, per sulphur atom, of similar strength are observed in derivatives of (3). These long contacts between dimers of (2; R = H) produce a two dimensional network. While (1) is observed to be planar in the gas phase, the solid state structure of (2; R = H) shows the nitrogen atom displaced from the plane by *ca.* 11°, at a distance of 0.186(2) Å from the mean plane, implying greater localisation of the unpaired electron on the nitrogen centre in the dimer.

^{||} *Crystal data:* $\text{C}_6\text{H}_4\text{S}_2\text{N}$, $M = 154.233$, orthorhombic, space group $Pbca$, $a = 7.6929(3)$, $b = 16.0396(7)$, $c = 10.3863(5)$ Å, $U = 1281.6(2)$ Å³, $Z = 8$, $D_c = 1.599$ Mg m⁻³. Data were collected on an Enraf-Nonius CAD-4 automated diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) using ω scans ($2\theta_{\text{max}}$ of 50°). The structure was solved by direct methods²⁰ and refined by full matrix least squares²¹ to residuals of $R = 0.030$, $R_w = 0.039$ (0.037, 0.039 including unobserved reflections) for 923(1111) reflections and 99 variables.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

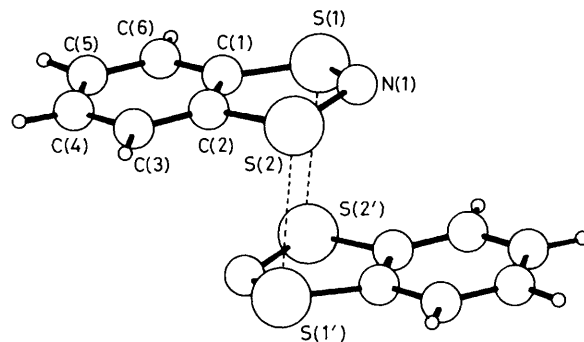


Figure 1. PLUTO view of the dimer unit of benzo-1,3,2-dithiazolyl (2; R = H). Selected bond lengths (Å) and angles (°) are: S(1)-N(1) 1.644(2), S(1)-C(1) 1.740(2), S(2)-N(1) 1.648(2), S(2)-C(2) 1.746(2), C(1)-C(2) 1.394(3), C(2)-C(3) 1.393(3), C(3)-C(4) 1.378(4), C(4)-C(5) 1.391(4), C(5)-C(6) 1.374(4), C(1)-C(6) 1.391(3), S(1)-S(2') 3.174(9); S(1)-N(1)-S(2) 113.9(1), N(1)-S(1)-C(1) 99.4(1), N(1)-S(2)-C(2) 99.1(1), S(1)-C(1)-C(2) 112.9(2), S(2)-C(2)-C(1) 113.1(2).

The greater thermal stability of (1) over other non-sterically hindered organic radicals including (2; R = H) [m.p. 85 °C (decomp.)] is surprising, especially in view of the inherent thermodynamic instability of S-N compounds. Interestingly, derivatives of (1) with CF_3 replaced by H and/or Me have very short lifetimes and we have found that their preparation at high concentration leads to decomposition *via* a number of radical species to a variety of diamagnetic products [*cf.* stability of $(\text{CF}_3)_2\text{NO}$ relative to $(\text{CH}_3)_2\text{NO}$]. The thermodynamic instability of the 1,3,2,4-dithiadiazolyl radical system (5), with respect to the isomeric 1,4,2,3-dithiadiazolyl (3) has recently been shown by its facile quantitative rearrangement reaction.²² Our proposal of a π^* - π^* dimer intermediate, in a head-to-tail conformation, is supported by the solid state structure of (2; R = H). By analogy, we might expect a similar rearrangement for the 1,3-dithiazolyl system (1) and (2; R = H) to give the thermodynamically more stable, isomeric 1,2,3-dithiazolyl (6) [derivatives of (6) have been extensively studied by Mayer²³]. The reluctance of (1) and (2; R = H) to undergo such a process may be understood by examination of the solid state structure of (2; R = H). The displacement of the nitrogen atoms out of the molecular plane, away from the other molecule in the dimer, probably prevents the formation of the new C-N bond required in the aforementioned rearrangement. The observed decomposition of derivatives of (1) to diamagnetic species must occur *via* a pathway of lower energy than the rearrangement to (6).

The non-sterically hindered radicals O_2 , NO, and $(\text{CF}_3)_2\text{NO}$, are thermodynamically stable by virtue of their high bond strength (O_2 , 119; NO, 151 kcal mol⁻¹) relative to weak σ -bonds (O-O, 34; N-N, 38; N-O, 39 kcal mol⁻¹) involved in conventionally σ -bonded dimers and oligomers. $2p\pi$ - $2p\pi$ bonds are maximised in these diatomics. Consequently, NO dimerises in liquid and solid state *via* a π^* - π^* interaction between the SOMOs, rather than an N-N or O-O σ -bond. A similar situation exists for (1), (2), (3), and related radicals, which maximise $2p\pi$ - $3p\pi$ bonding even at the expense of π^* -occupation. The π^* - π^* dimer is again favoured over the σ -bonded arrangement involving weak N-N or S-S (valence bond structures using only s and p orbitals) single bonds. The S-S bond is comparable to or weaker than the N-N bond and considerably weaker than S-S in S_8 . Stabilisation of $3p\pi$ - $3p\pi$ bonds in the main group by means of large substituents [*e.g.* $(\text{Me}_3\text{Si})_3\text{CP}=\text{PC}(\text{Me}_3\text{Si})_3$]²⁴ has attracted much attention. The existence of non-sterically hindered

$n\pi-n\pi$ bonds ($n > 2$) in M_4^{2+} ($M = S, Se, Te$), $S_2I_4^{2+}$, Br_2^+ , I_2^+ , I_4^{2+25} and related species can be rationalised using similar arguments to those presented above.

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References

- 1 A. F. Wells, 'Structural Inorganic Chemistry,' Clarendon Press, Oxford, 1984.
- 2 D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1976, **9**, 13.
- 3 M. Ballester, *Acc. Chem. Res.*, 1985, **18**, 380.
- 4 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' John Wiley & Sons, New York, 1980.
- 5 P. M. Spaziante, MTP International Review of Science, Inorganic Chemistry, 1972, **3**, 141.
- 6 A. K. Hoffmann and A. T. Henderson, *J. Am. Chem. Soc.*, 1961, **83**, 4671.
- 7 S. A. Fairhurst, R. S. Pilkington, and L. H. Sutcliffe, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 925.
- 8 Prepared and identified (e.s.r.) in solution, S. R. Harrison, R. S. Pilkington, and L. H. Sutcliffe, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 669.
- 9 Prepared and isolated as a pure crystalline solid, G. Wolmershäuser, M. Schnauber, and T. Wilhelm, *J. Chem. Soc., Chem. Commun.*, 1984, 573.
- 10 A. Vegas, A. Perez-Salazar, A. J. Banister, and R. G. Hey, *J. Chem. Soc., Dalton Trans.*, 1980, 1812; H.-U. Höfs, J. W. Bats, R. Gleiter, G. Hartmann, R. Mews, M. Eckert-Maksic, H. Oberhammer, and G. M. Sheldrick, *Chem. Ber.*, 1985, **118**, 3781.
- 11 M.-H. Whangbo, R. Hoffmann, and R. B. Woodward, *Proc. R. Soc. London, Ser. A*, 1979, **366**, 23.
- 12 G. K. MacLean, J. Passmore, M. N. S. Rao, M. J. Schriver, P. S. White, D. Bethell, R. S. Pilkington, and L. H. Sutcliffe, *J. Chem. Soc., Dalton Trans.*, 1985, 1405.
- 13 C. F. Krespan, *J. Am. Chem. Soc.*, 1961, **83**, 3434.
- 14 W. L. Jolly, 'The Synthesis and Characterisation of Inorganic Compounds,' Prentice-Hall Inc., Englewood Cliffs, N. J. 1970, p. 369.
- 15 P. W. Selwood, 'Magnetochemistry,' Interscience, New York, 1956, p. 107.
- 16 M. P. Murchie, Ph.D. Thesis, University of New Brunswick, 1986.
- 17 W. D. Blackley and R. R. Reinhard, *J. Am. Chem. Soc.*, 1965, **87**, 802.
- 18 W. V. F. Brooks, N. Burford, J. Passmore, M. J. Schriver, and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1986, following communication.
- 19 H. Oberhammer, 'Molecular Structure by Diffraction Methods,' The Chemical Society, London, 1976, vol. 4, p. 24.
- 20 P. Main, MULTAN-80 A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, York, 1980.
- 21 E. J. Gabe, F. L. Lee, and Y. LePage in Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases, eds. G. M. Sheldrick, C. Kruger, and R. Goddard, Clarendon Press, Oxford, 1985, pp. 167—174.
- 22 N. Burford, J. Passmore, and M. J. Schriver, *J. Chem. Soc., Chem. Commun.*, 1986, 140.
- 23 R. Mayer, G. Domischke, S. Bleisch, J. Fabian, A. Barth, and A. Stasko, *Coll. Czech, Chem. Commun.*, 1984, **49**, 684.
- 24 A. H. Cowley, *Acc. Chem. Res.*, 1984, **17**, 386.
- 25 J. Passmore, G. Sutherland, and P. S. White, *Inorg. Chem.*, 1982, **21**, 2717, and references therein; J. Passmore, G. Sutherland, T. Whidden, and P. S. White, *J. Chem. Soc., Chem. Commun.*, 1980, 289; A. J. Edwards, G. R. Jones, and R. J. C. Sills, *ibid.*, 1968, 1527; C. G. Davies, R. J. Gillespie, P. R. Ireland, and J. M. Sowa, *Can. J. Chem.*, 1979, **52**, 2048; R. J. Gillespie, R. Kapoor, R. Faggiani, C. J. Lock, M. Murchie, and J. Passmore, *J. Chem. Soc., Chem. Commun.*, 1983, 8.