Paramagnetic Liquids: The Preparation and Characterisation of the Thermally Stable Radical $Bu^t\overline{CNSNS}\cdot$ and its Quantitative Photochemically Symmetry Allowed Rearrangement to a Second Stable Radical $Bu^t\overline{CNSSN}\cdot$

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The new thermally stable paramagnetic liquid 5-t-butyl-1,3,2,4-dithiadiazolyl has been isolated in the dark and quantitatively photochemically isomerised to the paramagnetic liquid 5-t-butyl-2,3,1,4-dithiadiazolyl (non-systematic numbering for ease of comparison).

Thermally stable, neutral, free-radical, non-metal compounds can be categorised by the state of lowest energy in which they remain substantially paramagnetic. (i) Paramagnetic solids:† radicals which are paramagnetic in all states. These include the sterically hindered radicals such as diphenylpicrylhydrazyl (DPPH),[3] $(C_6Cl_5)_3C$,[4] and the non-sterically hindered O_2 and ClO_2.[5] (ii) Paramagnetic liquids: radicals which are diamagnetic dimers in the solid state but are extensively dissociated upon melting, *e.g.* $Bu^t{}_2NO$,[6] $(CF_3)_2NO$,[7] and $CF_3\overline{CSNSC}CF_3$.[8] (iii) Paramagnetic gases: radicals which are largely dimeric in the condensed phases and only extensively dissociated in the gas phase, *e.g.* NO,[9] NO_2.[5]

Compounds of type (ii) are rare. However, we have recently reported the first example of a C–S–N heterocyclic paramagnetic liquid (**1**), which is not sterically restricted from dimerising.[8] This followed Sutcliffe's initial discovery of the high stability of radicals of this nature in solution and their reluctance to dimerise.[10] We now report the preparation, isolation, and characterisation of two more paramagnetic liquids, 5-t-butyl-1,3,2,4-dithiadiazolyl (**2a**) and 5-butyl-2,3,1,4-dithiadiazolyl (**3a**).

A variety of derivatives of (**2**) (R = CH_3, CF_3, I)[11,12] and (**3**) (R = CH_3,[12] CF_3,[13] I,[12] Ph[14]) have been previously reported.

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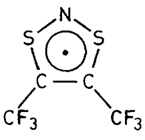
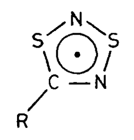
† There are a number of examples of ionic paramagnetic solids, *e.g.* salts containing $O_2{}^+$,[1] $O_2{}^-$,[1] $I_2{}^+(Sb_2F_{11}{}^-)$,[1] $C_6F_6{}^+$.[2]

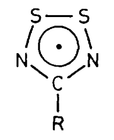


(1)



(2)

a; R = Bu^t

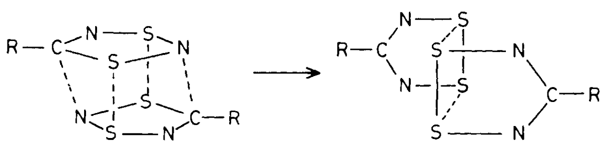


(3)

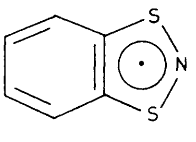
a; R = Bu^t

However, compounds (**2a**) and (**3a**), containing the t-butyl group, have unusual properties. For example, (**3a**) has an uncharacteristically low melting point, for this class of disulphides, which has allowed the identification of (**3a**) as a paramagnetic liquid. In addition, (**2a**) is thermally stable with respect to isomerisation[12] to (**3a**). On this basis, we have discovered that the facile quantitative isomerisation[12] is 'thermally symmetry forbidden' and 'photochemically symmetry allowed.'[15] $\mathrm{Bu^t\overline{CNSNS}AsF_6}$ (3.27 mmol) (prepared by the published method[11,12]) reacted with $\mathrm{SbPh_3}$ (2.25 mmol) and $\mathrm{NMe_4Cl}$ (5.51 mmol) in $\mathrm{SO_2}$ (7.19 g) for 10 min to form a black-purple solution (all manipulations were performed in the dark). The volatile products were fractionated through a series of U-tube traps at −10 and −196 °C under a dynamic vacuum. The brown-black liquid collected at −10 °C was identified as compound (**2a**) (2.86 mmol, 87%, m.p. 0—1 °C), by i.r. and e.s.r. spectroscopy ($g = 2.0071$, $a^{\mathrm{N2}} = 1.09$ mT, $a^{\mathrm{N4}} = 0.06$ mT; *cf.* other derivatives),[12] and magnetic susceptibility. The pure brown liquid was left at room temperature exposed to normal room light for 5 days resulting in a colour change to a red-purple liquid which was purified by fractional distillation (as above) to give pure compound (**3a**) [2.58 mmol, 90% based on (**2**), m.p. 20—21 °C]. Compound (**3a**) was characterised by i.r. and e.s.r. spectroscopy ($g = 2.0121$, $a^{\mathrm{N}} = 0.52$ mT; *cf.* other derivatives[12]), elemental analysis, and magnetic susceptibility. Unlike (**2**; R = $\mathrm{CH_3}$) which could only be isolated in small quantities, at low temperature,[12] (**2a**) can be stored in the dark at room temperature for at least 20 h without any observable (e.s.r.) rearrangement to (**3a**). In $\mathrm{CFCl_3}$ solution (**2**; R = $\mathrm{CH_3}$) isomerises almost completely within a week when exposed to room light. However, in the dark minimal (<5%) isomerisation is observed after a month. Compound (**2a**) appears to be indefinitely stable in solution when stored in the dark.

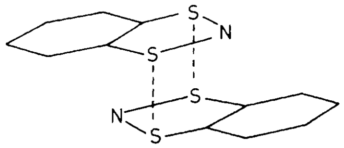
The preparation and purification of relatively large quantities of (**2**) now provides a means for the ready exploration of the chemistry of this heterocyclic framework. Moreover, the controlled isomerisation of (**2**) allows quantitative synthesis of a wide variety of derivatives of (**3**). The transformation of one radical species into another in a quantitative fashion is unprecedented, and is particularly surprising in view of the kinetic and thermodynamic instability associated with free radicals. A concerted process is implied, and our postulated head-to-tail π^*–π^* dimer intermediate (A)[12] is supported by the *X*-ray crystal structure of the related dithiazolyl compound (**4**), showing the same conformation (**5**).[8] The centre of symmetry, *i*, existing in the dimer structure (A) and the π^*–π^* dimer structure of the product disulphide (**3**), (B), will be retained throughout the concerted rearrangement. Therefore we have examined the electronic structure of the hypothetical hydrogen derivatives of (A) and (B) (CNDO). Of the 27 occupied MOs (valence electrons only), (A) has 14 that are symmetric (g) with respect to *i*, while (B) has only 13 MOs having g symmetry (*i.e.* 14 occupied MOs have u symmetry). Consequently, correlation of the MOs of (A) and (B) with respect to *i* involves a cross-over correlation between an occupied MO of (A) and an unoccupied MO of (B). This renders the process 'thermally symmetry forbidden' and 'photochemically symmetry allowed.'[15] While many of the occupied antibonding π–π interactions of (A) correlate with occupied low-lying weak σ^* S–S MOs of (B), the antibonding combination of the SOMO-1‡ MO of (**2**), illustrated in (**6**), correlates with a high energy unoccupied σ^* S–S MO of (B). Therefore, as the rearrangement proceeds and the new disulphide bonds are formed, the energy of (**6**) increases sharply owing to the large contribution at the sulphur centres in the SOMO-1. It is a balance of the π–π bonding MOs and an antibonding contribution related to (**6**) that is responsible for the long S–S dimer bonds observed in the solid state structures of (**3**) (R = $\mathrm{CF_3}$,[13] Ph[14]), described by Gleiter as a 4-centre 6e π–π interaction.[16]



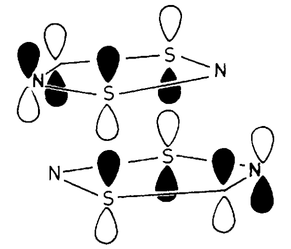
(A) (B)



(**4**)



(**5**)



(**6**)

Table 1. Magnetic susceptibility values[a] for $\mathrm{CF_3\overline{CSNSC}CF_3}$ (**1**) $\mathrm{Bu^t\overline{CNSNS}}$ (**2a**), and $\mathrm{Bu^t\overline{CNSSN}}$ (**3a**) in the pure liquid state and at infinite dilution.

Compound	χ_g/ ($\times 10^{-6}$ c.g.s.) pure liquid	$\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$	χ_g/ ($\times 10^{-6}$ c.g.s.) infinite dilution[b]
(**1**)	3.8	1.5	6.2
(**2a**)	5.1	1.5	9.5[c]
(**3a**)	4.8	1.4	9.5

[a] 10% error associated with all measurements. [b] Obtained by extrapolation.[8] [c] Assumed to be the same value as observed for (**3a**).

The magnetic moments of compounds (**2a**) and (**3a**) as liquids at 20 °C were determined by the Gouy method[17] using $\mathrm{Ni(en)_3S_2O_3}$ (en = ethylenediamine) as a standard. The observed magnetic susceptibilities are compared with that of (**1**) in Table 1. Like (**1**) (**3a**) is diamagnetic in the solid state.

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‡ SOMO-1: π-type MO of (**2**) next lower in energy to the SOMO.

Table 2. $\Delta H_{\text{dimerisation}}$ values for derivatives of (**3**) in $CFCl_3$ obtained by quantitative e.s.r. spectroscopy.

Compound (**3**), R	ΔH_d/ kJ mol^{-1}	M.p., t/°C
Ph[a]	-37 ± 2	[c]
CF_3[b]	$-37 + 3$	37
Bu^t[b]	-31 ± 10	20—21

[a] Ref. 19. [b] This work. [c] Solid at room temperature.

However, both (**2a**) and (**3**) are substantially paramagnetic as liquids indicating that the liquid consists largely of monomer units. Variable temperature (5—362 K) magnetic susceptibility measurements[18] on a pure sample of (**3a**) showed χ_g to be essentially independent of temperature in the liquid range. Variable temperature e.s.r. measurements on liquid samples of pure (**1**) (293—357 K), (**3a**) (293—361 K), and (**3**; R = CF_3)§ (303—341 K) in capillaries, also showed no change in the signal integration with change in temperature. Therefore it appears that the low μ_{eff} values observed are not due to a monomer/dimer equilibrium. It is conceivable that the values are less than those expected for one electron per molecule (obtained by extrapolation from solution measurements to be 1.96 μ_B) due to some spin-pairing mechanism between monomers, without involving dimer or oligomer formation. The high percentage of monomer implies a positive ΔG°_d value for the dimerisation process at room temperature, and consequently a small ΔH°_d. In fact, ΔH°_d for (**1**) is zero or positive in $CFCl_3$ solution. By comparison all derivatives of (**3**) have substantial ΔH°_d values (Table 2), consistent with compounds (**3**) (R = CF_3, Ph, or CH_3) being dimeric in the solid state at room temperature. Therefore the unique 'paramagnetic liquid' nature of (**3a**) and (**3**; R = CF_3) is likely to be due to a large ΔS° value and all derivatives of (**1**), (**2**), and (**3**) are potential 'paramagnetic liquids.'

The existence of (**1**), (**2a**), and (**3a**) as 'paramagnetic liquids' at room temperature depends on the following. (i) The stability of the 7π heterocyclic radical monomer with respect to chemical decomposition. (ii) The reluctance of the π^*–π^* dimer to adjust to a conventionally σ-bonded N–N or S^+–S^+ alternative [for discussion with respect to (i) see ref. 8]. (iii) A weak π^*–π^* dimer bond. The π^*–π^* interactions have been used to describe dimerisation of the radical ions in $(S_3N_2{}^+)_2$,[20] $(C_2F_5SeSeC_2F_5{}^+)_2$,[21] $I_4{}^{2+}$,[22] $S_2O_4{}^{2-}$,[23] and $Se_2I_4{}^{2+}$,[23] and the unusual structure of $S_2I_4{}^{2+}$.[24] It is also likely to be responsible for the dimerisation of NO in the solid state,[5] the dimerisation of those nitroxides that are diamagnetic in the solid state (*cf.* Frémy's salt[1]), and the cross-ring interactions in $S_8{}^{2+}$, $Se_8{}^{2+}$,[25] S_4N_4,[26] and related compounds. It is therefore an important class of bonding arrangement. Both the importance, and subtle nature of these weak π^*–π^* interactions, is further illustrated in a new class of materials, the 'paramagnetic liquids.'

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§ Compound (**3**; R = CF_3) is reported by Mews to be paramagnetic as a liquid, however, the data and degree of paramagnetism are not discussed.[13]