Solid-state Rearrangement of Some 1,3,2,4-Dithiadiazoles to Their 1,2,3,5 Analogues

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A variety of 1,3,2,4-dithiadiazoles [*m*- and *p*-$C_6H_4(\overline{CNSNS})_2$ and 1,3,5-$C_6H_3(\overline{CNSNS})_3$] undergo solid-state rearrangement to their 1,2,3,5-dithiadiazole analogues. This isomerisation process has been examined using differential scanning calorimetry, X-ray powder diffraction techniques and both infrared and electron-spin resonance spectroscopy. A common mechanism is proposed for the rearrangement, involving head-to-tail S • • • N and S • • • S interactions between dithiadiazole rings.

Interest has recently been centred on heterocyclic free-radical species as potential organic metals.[1–11] To this end we have prepared a variety of multi(dithiadiazoles), including *p*-$C_6H_4(\overline{CNSNS})_2$[10] **1**. Although this bis(1,3,2,4-dithiadiazole) is an insulator, it contains a polymeric array of neutral molecules interacting through secondary S • • • S and S • • • N contacts and is amongst the first extended systems[8–11] based on the thiazyl radical. Unlike most dithiadiazole radicals, this material is only slightly moisture sensitive (surviving for several days in the open atmosphere) and does not readily rearrange photochemically.

We have also shown that spin–spin exchange interactions occur in a variety of these multiradicals[12] in solution and the degree of exchange is temperature dependent, significant exchange occurring at, and above, room temperature. Similar results have also been observed in multi(1,2,3,5-dithiadiazole) systems, *e.g.* **2**, studied by Oakley and co-workers,[8,9] and also in bis(dithiazoles).[5] This type of spin–spin exchange can be thought to be analogous to that observed in bis(nitroxyl) radicals.[13,14]

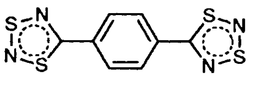
In addition to these solution properties, we have been able to isolate some of the 1,3,2,4-dithiadiazoles in the solid state; we now discuss their solid-state thermal stability.

Results and Discussion

Samples of *m*-$C_6H_4(\overline{CNSNS})_2$, 4,4′-$(\overline{SNSNC})C_6H_4$–$C_6H_4$-$(\overline{CNSNS})$ and *sym*-$C_6H_3(\overline{CNSNS})_3$ were prepared in a similar manner to the preparation of *p*-$C_6H_4(\overline{CNSNS})_2$, *i.e.* by reduction of the corresponding chloride salt in MeCN,[10] see equation (1). The corresponding free-radical precipitate was

$$[p\text{-}C_6H_4(\overline{CNSNS})_2]Cl_2 + SbPh_3 \longrightarrow SbPh_3Cl_2 + p\text{-}C_6H_4(\overline{CNSNS})_2 \quad (1)$$

then filtered off, washed and pumped to dryness. Fresh samples were prepared for each study (carried out within 24 h of preparation), but could be stored for some time (2–8 weeks) at room temperature in the absence of light, without significant degradation.



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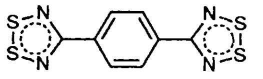

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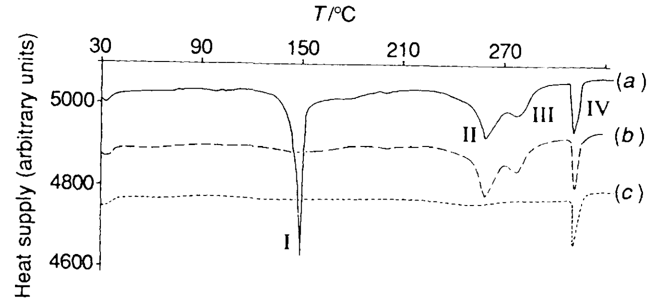


Fig. 1 Differential scanning calorimetry traces of (*a*) *p*-$C_6H_4(\overline{CNSNS})_2$, (*b*) *p*-$C_6H_4(\overline{CNSNS})_2$ after thermolysis to 170 °C, and (*c*) *p*-$C_6H_4(\overline{CNSNS})_2$ after thermolysis and extraction with CH_2Cl_2

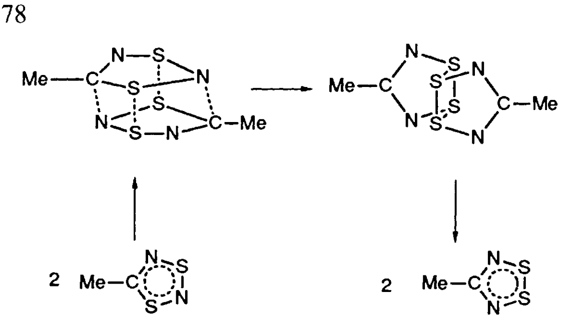
These radicals were then studied by differential scanning calorimetry (DSC). A typical DSC trace [that of *p*-C_6H_4-$(\overline{CNSNS})_2$] is shown in Fig. 1(*a*). In the case of *p*-$C_6H_4(\overline{CNSNS})_2$ the initial exotherm (I) (*ca.* 145 °C) is sudden and sharp, irrespective of heating rate, and this is attributed to rearrangement from the 1,3,2,4-dithiadiazole ring **1** to the 1,2,3,5-dithiadiazole analogue **2** [equation (2)]. This process

$$p\text{-}C_6H_4(\overline{CNSNS})_2 \xrightarrow{\text{heat, }150\ °C} p\text{-}C_6H_4(\overline{CNSSN})_2 \quad (2)$$

was observed to be irreversible; a sample heat treated to 170 °C failed to show a similar thermal event after cooling and reheating [see Fig. 1(*b*)].

Smaller exotherms (II and III) are due to by-products formed during the rearrangement process. Bulk-scale samples thermolysed to 150 °C and then purified by CH_2Cl_2 extraction showed no such exotherms, Fig. 1(*c*). At temperatures above 300 °C, decomposition of *p*-$C_6H_4(\overline{CNSSN})_2$ was observed in agreement with the literature observations.[8]

Infrared and elemental analyses of a heat-treated sample (thermolysed to 150 °C) of *p*-$C_6H_4(\overline{CNSNS})_2$ were in agreement with the literature data[8] for *p*-$C_6H_4(\overline{CNSSN})_2$. The heat of rearrangement, ΔH_{rearr}, was calculated at 317 ± 10 kJ mol^{-1}. The material also provided a change in solution ESR spectrum from



Scheme 1

a 1:1:1 triplet (g = 2.0057, a_N = 1.10 mT) to a 1:2:3:2:1 pentet (g = 2.011, a_N = 0.51). These data coupled with a change in the central g value for the solid-state radicals (g_{13} = 2.0051, g_{12} = 2.0102) are consistent with rearrangement from the 1,3-disulfur ring to the 1,2 isomer.

Bulk samples of *p*-$C_6H_4(CNSSN)_2$ could be obtained in *ca.* 75% recovered yield by thermolysing *p*-$C_6H_4(CNSNS)_2$ at 170 °C for 15 min, followed by CH_2Cl_2 extraction to remove small quantities of by-products, identified as *p*-$C_6H_4(CN)_2$ and S_4N_4 by infrared spectroscopy. Trace amounts of royal blue $(SN)_x$ could also be observed as a thin coating on the sides of the thermolysis vessel.

Mechanism.—Dithiadiazoles have been shown to be largely dissociated in solution[15] but Passmore and co-workers[16,17] have previously proposed that rearrangement from the 1,3,2,4-dithiadiazoles to their 1,2,3,5 isomers in solution is a bimolecular process (Scheme 1) which proceeds through a variety of intermolecular C • • • N and S • • • S interactions. Although dithiadiazoles tend to be associated in the solid state (frequently as dimers or oligomers[8–11,18–23]) and their chemistries frequently differ from those in solution, we can now provide the first evidence for the proposed solution mechanism.

The solid-state structure[10] of *p*-$C_6H_4(CNSNS)_2$ at 298 K is essentially planar with the dithiadiazole rings inclined at 5.4° to the phenylene plane and secondary interactions (S • • • N *ca.* 3.11 and S • • • S *ca.* 3.21 Å) between rings in different molecules, as shown in Scheme 2(*a*). This type of secondary interaction holds the rings in a polymeric array, with the individual units being held together in a head-to-tail arrangement.

A comparison of Schemes 1 and 2(*a*) shows the CNSNS rings in the solid-state structure of *p*-$C_6H_4(CNSNS)_2$ to be in a conformation almost identical to that proposed by Passmore and co-workers for the solution rearrangement of 1,3,2,4-dithiadiazoles to their 1,2,3,5 isomers. We may therefore consider that the solid-state rearrangement process observed in these materials occurs through the same mechanism as that in solution. However, the solid-state packing of *p*-$C_6H_4(CNSSN)_2$ observed by Oakley and co-workers[8] is not that of an infinite polymeric array, as in *p*-$C_6H_4(CNSNS)_2$, but of a regular packing of dimeric pairs Scheme 2(*d*). Consequently we propose that on thermal rearrangement the molecules initially retain the same relative positions as in *p*-$C_6H_4(CNSNS)_2$, Scheme 2(*a*), *i.e.* they retain the same space group as that of *p*-$C_6H_4(CNSNS)_2$. Subsequent lattice rearrangement and distortion then occurs to provide the dimeric structure as observed by Oakley and co-workers. The full solid-state transformation process can therefore be considered to proceed through three steps (probably concerted): isomerisation, followed by a shift along the lattice glide plane and then a lattice distortion to the dimeric structure (Scheme 2).

Attempts to isolate the intermediate layered 1,2 compound [Scheme 2(*b*)] were unsuccessful since the thermal energy, at *ca.* 150 °C, required to induce rearrangement is also more than sufficient to provide a shift along the glide plane, allowing dimerisation and lattice distortion to the structure in Scheme 2(*d*). This was verified by X-ray powder diffraction: data for the thermolysed product (Table 1) showed complete conversion from *p*-$C_6H_4(CNSNS)_2$ into *p*-$C_6H_4(CNSSN)_2$. The X-ray data were comparable with those of an authentic sample, with some extra weaker lines (< 10% intensity) consistent with the formation of smaller quantities of by-product.

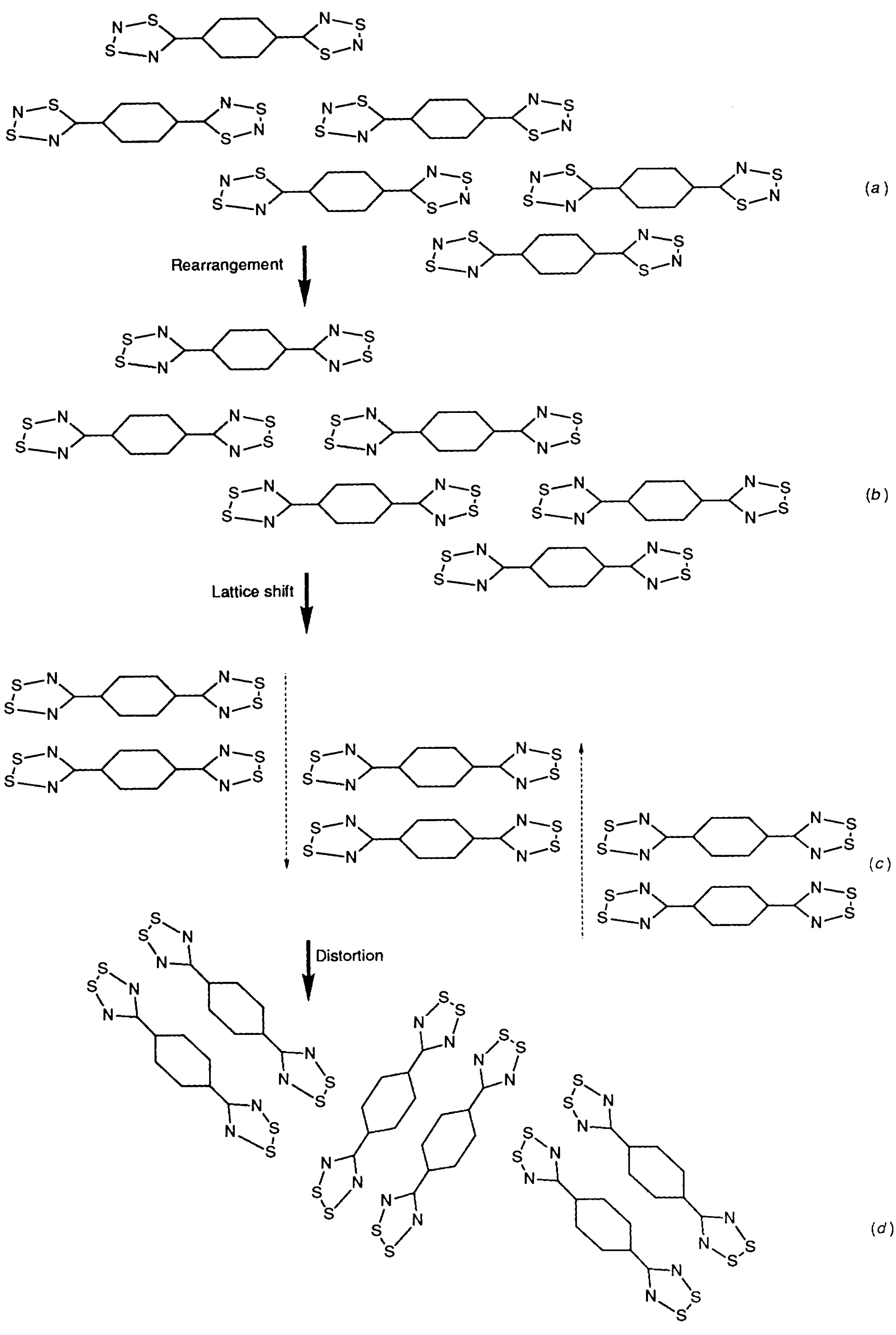
Fig. 2 shows DSC traces for *m*-$C_6H_4(CNSNS)_2$ and *sym*-$C_6H_3(CNSNS)_3$. Both of these materials show similar DSC traces to that oberved for *p*-$C_6H_4(CNSNS)_2$, although isomerisation occurred at 110 and 290 °C respectively. We propose that these materials also undergo similar rearrangements, with the implication that their solid-state packing is similar to that of *p*-$C_6H_4(CNSNS)_2$; the secondary interactions (S • • • S and S • • • N) between rings in these structures facilitating solid-state rearrangement.

In contrast, neither 4,4′-(SNSNC)C_6H_4–C_6H_4(CNSNS) [Fig. 2(*c*)] nor $(NC)_2C$–CNSNS shows such sharp exotherms even on heating to 400 °C. Although attempts to prepare single crystals of 4,4′-(SNSNC)C_6H_4–C_6H_4(CNSNS) have been unsuccessful (high-vacuum sublimation provided only small crystallites with a preferential alignment of the molecules along one of the crystal axes), crystals of $(NC)_2C$–CNSNS could be grown.[11] This dithiadiazole forms molecular planes of neutral molecules held together through in-plane CN • • • S interactions with no evidence of out-of-plane interactions of the type observed in *p*-$C_6H_4(CNSNS)_2$. Consequently we may consider the type of out-of-plane interactions observed in *p*-C_6H_4-$(CNSNS)_2$ to be of prime importance in the solid-state rearrangement, and provides strong evidence in support of the solution mechanism previously proposed.

Perhaps of greater synthetic interest is the observation that some salts of these dithiadiazolium cations can also undergo rearrangement. In particular iodides of these materials show similar sharp exothermic processes; infrared data for the thermolysed products are consistent with such a rearrangement process occurring in these solid-state samples also. Fig. 2 shows the DSC trace for [*p*-$C_6H_4(CNSNS)_2]I_2$; a smaller initial exotherm of varying intensity is initially observed (145 °C) (I) which is attributed to traces of *p*-$C_6H_4(CNSNS)_2$, already shown to isomerise at this temperature. The intensity of this band is dependent on the age of the sample and can be attributed to some decomposition, though loss of iodine, to the neutral *p*-$C_6H_4(CNSNS)_2$. (Decomposition of dithiadiazolium iodides has been known for some time and has been used as a convenient route in the synthesis of the corresponding dithiadiazoles.[24]) However a strong second exotherm (II) is also observed (195 °C) and is indicative of rearrangement of the iodide salt to its 1,2-isomeric counterpart. The thermal stability of these solid iodides at room temperature suggests that their slow decomposition under ambient conditions, in the solid state (to give the respective dithiadiazole and iodine) is probably a photochemical process.

Conclusion

The DSC, XRD and IR data indicate that the sharp exothermic processes observed for some 1,3,2,4-dithiadiazoles, and their salts, are due to solid-state isomerisation to their 1,2,3,5-dithiadiazole counterparts. Provided that the molecular packing facilitates out-of-plane intermolecular interactions, of the type discussed, we propose that this may be a general process for all solid-state 1,3,2,4-dithiadiazoles. This type of solid-state rearrangement process may prove useful in the synthesis of 1,2,3,5-dithiadiazoles that are not obtained readily by conventional synthesis.



Scheme 2

Experimental

All reactions and manipulations were carried out under an atmosphere of dry nitrogen and solvents were dried before use. Infrared spectra were recorded as Nujol mulls between KBr or CsI plates using a Perkin-Elmer 577 or 457 grating spectrophotometer, mass spectra by a VG Analytical 7070E spectrometer, ^{1}H and ^{13}C NMR spectra at 250 MHz on a Bruker AC250 spectrometer and ESR spectra on a Varian V-4502 EPR spectrometer. Carbon, H and N analyses were carried out on a Carlo-Erba 1106 elemental analyser.

Differential scanning calorimetry measurements were made on a Mettler FP85 thermal analysis cell coupled to a Mettler FP80 processing unit. Samples were hermetically sealed in aluminium capsules under nitrogen and heating was carried out under an argon shroud. Data collection and manipulation were carried out on an Opus PCIII with in-house software

Table 1 *d*-Spacing data

p-C$_6$H$_4$(CNSNS)$_2$				Heated p-C$_6$H$_4$(CNSNS)$_2$	p-C$_6$H$_4$(CNSSN)$_2$			
d_{hkl}(obs.)/Å (intensity)	*h*	*k*	*l*	d_{hkl}(obs.)/Å (intensity)	d_{hkl}(obs.)/Å (intensity)	*h*	*k*	*l*
				9.28 (m)	9.28 (m)	0	2	0
				8.33 (w)	8.33 (w)	0	0	1
7.32 (s)	0	0	1					
				6.51 (m)	6.51 (m)	0	2	1
5.94 (s)	0	1	0					
5.41 (vs)	1	0	0	5.41 (vs)	5.41 (vs)	-1	0	1
					5.17 (w)	-1	1	1
				5.14 (m)				
				4.92 (w)	4.92 (w)	1	2	0
4.80 (m)	1	1	0					
4.33 (s)	1	1	1		4.33 (w)	1	1	1
				4.19 (w)	4.19 (w)	0	4	1
				4.12 (w)	4.12 (w)	0	2	2
				4.06 (w)	4.06 (w)	-1	3	1
3.74 (m)	0	1	2					
				3.70 (s)	3.70 (s)	-1	2	2
				3.65 (s)	3.65 (s)	1	3	1
					3.48 (m)	-1	4	1
				3.41(s)				
3.36 (vs)	0	1	2					
3.33 (vs)	0	1	2					
3.29 (vs)	0	1	2					
				3.28 (vs)	3.28 (vs)	1	0	2
				3.24 (vs)	3.24 (vs)	1	1	2
3.22 (vs)	-1	1	1					
					3.14 (w)	1	5	0
3.10 (w)	1	1	2		3.10 (w)	1	2	2
3.02 (m)	1	2	0					
				2.91 (m)	2.91 (m)	1	3	2
				2.88 (w)	2.88 (m)	1	5	1
2.82 (w)	2	1	0					
2.75 (w)	-1	-1	2	2.75 (m)	2.75 (m)	2	2	0
2.72 (w)	2	0	0					
				2.71 (s)	2.71 (s)	-1	6	1
2.62 (w)	2	0	1					
				2.58 (m)	2.58 (s)	0	6	2
2.53 (w)	1	-1	2					
2.49 (w)	1	2	2					
2.44 (w)	0	0	3					
				2.41 (w)				
2.40 (w)	2	2	0					
2.37 (w)	2	2	0					
					2.35 (w)	0	8	0
2.27 (w)	1	0	3					
2.15 (w)	2	-1	1					
2.12 (w)	2	2	2					
				2.08 (w)	2.08 (w)	1	5	3
				2.04 (w)	2.04 (w)	-2	6	2
				1.95 (w)	1.95 (w)	-1	5	4
				1.92 (w)	1.92 (w)	3	0	0
				1.91 (w)	1.91 (w)	-3	2	1
1.90 (w)	-2	1	2					
1.88 (w)	3	1	0					
				1.84 (w)	1.84 (w)	1	4	4
					1.83 (w)	-2	4	4
					1.81 (w)	3	0	1
				1.77 (w)	1.77 (w)	3	4	0
1.73 (w)	-3	0	1					
				1.71 (w)	1.71 (m)	-3	3	3

(J. Rawson, 1991) and printed on an Epson LQ-850+ dot-matrix printer.

X-Ray powder photographs of silicone oil mulls of the radicals were carried out using a Guinier de Wolff Camera No. II (Enraf–Nonius, Delft) (Cu-Kα radiation, λ = 1.5418 Å) and recorded on Agfa-Gevaert Osray X-ray film. The *hkl* values were assigned by comparison with values predicted from crystal structure unit-cell parameters using a computer program to generate indexed d_{hkl} values.[25]

Materials.—The salt [SNS]AsF$_6$ was prepared according to the literature method[26] with some amendments[11]; [NBu$_4$]Cl and [NBu$_4$]I (Lancaster) were precipitated twice from acetone by addition of diethyl ether, followed by baking at 75 °C *in vacuo*. 4,4′-Dicyanobiphenyl (Lancaster), m-C$_6$H$_4$(CN)$_2$ Aldrich) and *sym*-C$_6$H$_3$(CN)$_3$ (Alfred Bader) were purified by sublimation *in vacuo*. [m- and p-C$_6$H$_4$(CNSNS)$_2$][AsF$_6$]$_2$ and p-C$_6$H$_4$(CNSNS)$_2$ were prepared according to the literature

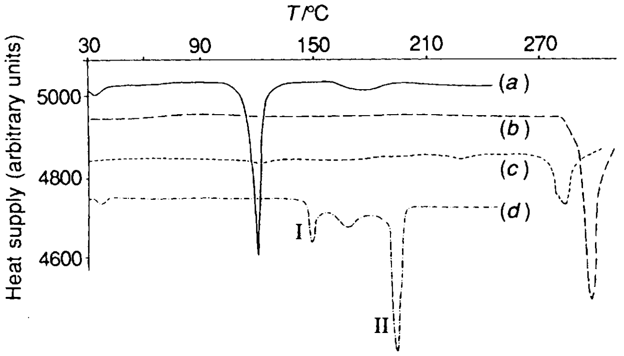


Fig. 2 Differential scanning calorimetry traces for (*a*) *m*-C_6H_4-(CNSNS)$_2$, (*b*) *sym*-C_6H_3(CNSNS)$_3$, (*c*), 4,4′-(SNSNC)C_6H_4–C_6H_4(CNSNS), and (*d*) [*p*-C_6H_4(CNSNS)$_2$]I_2

method.[10] Other materials were used without further purification.

Preparations.—[4,4′-(SNSNC)C_6H_4–C_6H_4(CNSNS)][AsF_6]$_2$. The compound 4,4′-NCC_6H_4–C_6H_4CN (0.170 g, 0.832 mmol) and [SNS]AsF_6 (0.445 g, 1.67 mmol) were stirred in liquid SO_2 for 36 h to yield an orange precipitate under a dark orange solution. The crude product was filtered off and washed three times with CH_2Cl_2 (5 cm^3). Yield 0.4839 g, 79%. IR ν_{max}/cm^{-1}: 1605s, 1498m, 1418s, 1400s, 1337m, 1212w, 1197mw, 1150w, 1025w, 1007w, 983vs, 915w, 890w, 830ms, 817m, 800s, 700vs (br), 650m, 632m, 585m, 575w, 437m and 400s. ^1H NMR (CD_3CN): δ 8.49 (d, 4 H) and 8.20 (d, 4 H). Electron impact (EI) mass spectrum: *m/z* 282 ($SNSNCC_6H_4$–C_6H_4CN, 100), 236 ($NSNCC_6H_4$–C_6H_4CN, 10.5), 204 (NCC_6H_4–C_6H_4CN, 71), 178 (C_6H_4–C_6H_4CN, 4), 177 (C_6H_3–C_6H_4CN, 8), 176 (C_6H_2–C_6H_4CN, 7), 152 (C_6H_4–C_6H_4, 2), 151 (C_6H_3–C_6H_4, 4), 78 (S_2N_2, 12.5) and 46 (SN, 7%) (Found: C, 22.30; H, 1.05; N, 7.50. Calc. for $C_{14}H_8As_2F_{12}N_4S_4$: C, 22.75; H, 1.10; N, 7.60%).

[4,4′-(SNSNC)C_6H_4–C_6H_4(CNSNS)]Cl_2. The compound [4,4′-(SNSNC)C_6H_4–C_6H_4(CNSNS)][AsF_6]$_2$ (0.331 g, 0.5 mmol) and a slight excess of [NBu_4]Cl (0.2775 g, 1.26 mmol) were stirred in CH_2Cl_2 for 24 h to produce an orange precipitate under a pale solution. The crude product was filtered off and washed three times with CH_2Cl_2 (8 cm^3) by back-condensation. Yield 0.150 g, 70%. IR ν_{max}/cm^{-1}: 1600s, 1410s, 1337s, 1280w, 1255w, 1217w, 1197m, 1028w, 1003w, 983vs, 922w, 872m, 828s, 780s, 717m, 680m, 648m, 633w, 625m, 580ms and 418s (Found: C, 39.35; H, 1.90; N, 13.00. Calc. for $C_{14}H_8Cl_2N_4S_4$: C, 38.95; H, 1.85; N, 13.00%).

4,4′-(SNSNC)C_6H_4–C_6H_4(CNSNS). The compound [4,4′-(SNSNC)C_6H_4–C_6H_4(CNSNS)]Cl_2 (0.431 g, 1 mmol) and $SbPh_3$ (0.3528 g, 1 mmol) were stirred in MeCN for 3 h, to yield a dark precipitate under a green-brown solution. The solubles were filtered off and the brown product washed with MeCN (3 × 5 cm^3). Yield 0.273 g, 76%. IR ν_{max}/cm^{-1}: 1610m, 1402s, 1235m (br), 1190w, 1133w, 1117w, 1005mw, 933s, 865m, 820s, 782s, 737m, 717s, 700s, 660m, 645mw, 630w, 595s, 545mw, 345w and 315mw (Found: C, 46.60; H, 2.20; N, 15.50. Calc. for $C_{14}H_8N_4S_4$: C, 46.65; H, 2.20; N, 15.55%). ESR: 1:1:1 triplet (a_N = 1.10 mT); also bands at $a_N/2$ due to spin–spin exchange at room temperature.

[*m*-C_6H_4(CNSNS)$_2$]Cl_2. The compound [*m*-C_6H_4-(CNSNS)$_2$][AsF_6]$_2$ (330 mg, 0.5 mmol) and NBu_4Cl (280 mg, 1.01 mmol) were stirred in MeCN for 20 min to give a bright yellow precipitate. Following removal of the supernatant by filtration, the crude product was washed repeatedly with back-distilled solvent and dried *in vacuo*. Yield: 141 mg, 0.40 mmol, 80%. IR ν_{max} cm^{-1}: 1600w, 1420m, 1400s, 1330w, 1295w, 1250w (br), 1190w, 1180 (sh), 1095w (br), 1030w, 990w, 980w, 940w, 915w, 875m, 830w, 825w, 785m, 775m, 690w, 680 (sh), 670w, 660w, 650w, 605w, 580w, 570m, 460w (br), 435w, 415s and 400w (Found: C, 27.40; H, 1.35; N, 15.85. Calc. for $C_8H_4Cl_2N_4S_4$: C, 27.05; H, 1.15; N, 15.75%).

m-C_6H_4(CNSNS)$_2$. The compound [*m*-C_6H_4(CNSNS)$_2$]Cl_2 (118 mg, 0.33 mmol) and excess of $SbPh_3$ were stirred in MeCN for 4 h to give a dark brown-black precipitate. The supernatant was filtered off, and residual $SbPh_3$ and $SbPh_3Cl_2$ were removed by repeated washing with back-distilled solvent. The product was dried *in vacuo*. Yield: 55 mg, 0.19 mmol, 59%. IR ν_{max}/cm^{-1}: 1600w (br), 1500 (sh), 1425 (sh), 1440s, 1190 (sh), 1180w, 1100w, 1018w, 1010 (sh), 920w, 885 (sh), 880w, 832w, 790m, 780s, 770w, 720m, 705s, 670m, 650w, 640 (sh), 580w, 540w (br) and 460w (br). EI Mass spectrum: *m/z* 284 (M^+, 84), 238 ($[M - SN]^+$, 26), 206 ($[M - S_2N)]^+$, 84), 160 {$[M - (S_2N + SN)]^+$, 28}, 128 ($[M - 2S_2N]^+$, 29), 102 ($[C_6H_4CN]^+$, 15), 78 ($[S_2N]^+$, 100), 64 ($[S_2]^+$, 25) and 46 ($[SN]^+$, 43%) (Found: C, 33.05; H, 1.45; N, 19.35. Calc. for $C_8H_4N_4S_4$: C, 33.80; H, 1.40; N, 19.70%).

[*p*-C_6H_4(CNSNS)$_2$]I_2. The compound [*p*-C_6H_4(CNSNS)$_2$][AsF_6]$_2$ (217 mg, 0.33 mmol) and [NBu_4]I (247 mg, 0.67 mmol) were stirred in MeCN for 24 h at room temperature to give the product as a black microcrystalline precipitate. Following removal of solvent the crude product was washed repeatedly with CH_2Cl_2 and then SO_2. Finally it was washed continuously for 3 d in a closed extractor by cycling CH_2Cl_2 under vacuum, and dried *in vacuo*. Yield: 105 mg, 0.20 mmol, 59%. IR ν_{max}/cm^{-1}: 1510w, 1440 (sh), 1433 (sh), 1392 (sh), 1315w, 1295w, 1240w, 1125w, 962s, 920m, 835m, 800m, 745s, 720w, 662w, 613m, 570m, 455w (br), 410m, 400m and 390w. (Found: C, 17.80; H, 0.75; N, 10.35. Calc. for $C_8H_4I_2N_4S_4$: C, 17.85; H, 0.75; N, 10.40%). EI Mass spectrum: *m/z* 284 ($[S_2N_2CC_6H_4CN_2S_2]^+$, 35), 254 ($[I_2]^+$, 75), 206 ($[S_2N_2CC_6H_4CN]^+$, 100), 160 ($[SNCC_6H_4CN]^+$, 18), 128 ($[NCC_6H_4CN]^+$, 28), 127 ($[I]^+$, 53), 102 ($[C_6H_4CN]^+$, 7), 78 ($[S_2N]^+$, 100), 64 ($[S_2]^+$, 28) and 46 ($[SN]^+$, 45%).

[*sym*-C_6H_3(CNSNS)$_3$][AsF_6]$_3$. 1,3,5-Tricyanobenzene (153 mg, 1.0 mmol) and [SNS][AsF_6] (801 mg, 3.0 mmol) were stirred in liquid SO_2 at room temperature for 5 d to give the product as a colourless crystalline precipitate. Following removal of solvent the product was washed clean of coloured impurities with a small amount of SO_2, and then by exhaustive washing with CH_2Cl_2. It was dried *in vacuo*. Yield: 668 mg, 0.70 mmol, 70%. IR ν_{max}/cm^{-1}: 3040w, 1608m, 1397s, 1330w, 1280w, 1200m, 1150w, 1080 (sh), 1065m, 945m, 910 (sh), 895m, 800s, 720vs (br), 610w, 582m, 572 (sh), 440ms and 390vs. NMR (CD_3CN): ^1H, δ 9.46 (s); ^{13}C, δ 128.8, 137.8 (aryl C) and 200.3 (CNSNS) (Found: C, 11.20; H, 0.35; N, 8.60. Calc. for $C_9H_3As_3F_{18}N_6S_6$: C, 11.30; H, 0.30; N, 8.80%).

[*sym*-C_6H_3(CNSNS)$_3$]Cl_3. The compound [*sym*-C_6H_3-(CNSNS)$_3$][AsF_6]$_3$ (318 mg, 0.33 mmol) and [NBu_4]Cl (278 mg, 1.0 mmol) were stirred in MeCN for 1 h to give the product as a bright yellow precipitate. The supernatant was filtered off and the product washed repeatedly with back-distilled solvent, followed by drying *in vacuo*. Yield: 123 mg, 0.25 mmol, 75%. IR ν_{max}/cm^{-1}: 1395s, 1340w, 1310w (br), 1278w, 1217 (sh), 1200w, 1182 (sh), 1117w (br), 1065w, 990 (sh), 985w, 963s, 932w, 920m, 855s, 823w, 775s, 770m, 697m, 680w, 668w, 652m, 580s, 510w (br), 475m, 413s and 375w (Found: C, 21.55; H, 0.70; N, 16.85. Calc. for $C_9H_3Cl_3N_6S_6$: C, 21.85; H, 0.6; N, 17.00%).

sym-C_6H_3(CNSNS)$_3$. The compound [*sym*-C_6H_3-(CNSNS)$_3$]Cl_3 (0.493 mg, 1 mmol) and a slight excess of $SbPh_3$ (0.564 mg, 1.6 mmol) were placed in one limb of a two-limbed reaction vessel. Acetonitrile (8 cm^3) was introduced into the other leg before vacuum transfer onto the reaction mixture. On addition of the solvent a rapid darkening occurred, and a brown-black precipitate formed. The mixture was stirred for 15 min to ensure complete reaction, after which time the supernatant was removed by filtration and the product washed repeatedly with back-distilled solvent. The brown-black product was dried *in vacuo*. Yield: 0.240 g, 62%. IR ν_{max}/cm^{-1}: 3160 (sh), 3030 (sh), 1680w (br), 1595w, 1490m, 1440s, 1415m, 1310w, 1290w, 1185m, 1068w, 1050 (sh), 1035 (sh), 992w, 920 (sh), 915w, 905 (sh), 892w, 880w, 853w, 835 (sh), 830w, 795s, 760w, 740w, 720s, 705s, 695s, 663s, 638w, 570w, 545 (sh), 540m and 390w (Found: C, 27.70; H, 0.80; N, 21.55. Calc. for $C_9H_3N_6S_6$: C, 27.90; H, 0.80; N, 21.15%).

[*sym*-C_6H_3(CNSNS)$_3$]I_3. The compound [*sym*-C_6H_3-(CNSNS)$_3$][AsF_6]$_3$ (318 mg, 0.33 mmol) and [NBu$_4$]I (369 mg, 1.0 mmol) were stirred for 24 h in MeCN (8 cm^3) at room temperature to give a black microcrystalline precipitate. After removal of the supernatant by filtration the crude product was transferred to a closed extractor and washed for 24 h with cycling CH_2Cl_2. The purified product was dried *in vacuo*. Yield: 200 mg, 0.26 mmol, 79%. IR ν_{max}/cm^{-1}: 1390 (sh), 933w, 925 (sh), 905w, 825m, 785w, 740w, 660w, 640w, 567s, 510w, 460w, 395s and 365w. EI Mass spectrum: *m*/*z* 387 (M^+, 20), 341 ([M − SN]$^+$, 5), 309 ([M − S_2N]$^+$, 79), 263 {[M − (S_2N + SN)]$^+$, 24}, 231 ([M − 2S_2N]$^+$, 60), 185 {[M − (2S_2N + SN)]$^+$, 16}, 153 ([M − 3S_2N]$^+$, 18), 78 ([S_2N]$^+$, 100), 64 ([S_2]$^+$, 38) and 46 ([SN]$^+$, 42); M denotes *sym*-$C_6H_3(CN_2S_2)_3$ (Found: C, 13.85; H, 0.40; N, 10.90. Calc. for $C_9H_3I_3N_6S_6$: C, 14.05; H, 0.40; N, 10.95%).

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