Novel Bonding Geometry and Valence Tautomerism of 4-(*N,N*-Dimethyldithiocarbamato)-2-dimethyliminio-1,3-dithietane Tetraphenylborate, $[Me_2NCS_2{\cdot}CH{\cdot}S_2CNMe_2]^+Ph_4B^-$

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A ring-opening/ring-closing tautomerism in solution of the title compound is deduced from the temperature dependence of the ^1H NMR spectra; the molecular structure found by X-ray crystal analysis is favourably oriented for this tautomerism.

N,N-Dialkyldithiocarbamato substituent groups exhibit interesting chemical properties such as 1,3-allylic rearrangements,[1–3] anchimerism[4] and neighbouring-group participation,[5] and also yield ambient cations when converted to cyclic iminium salts.[6] These characteristics have led us to design the title compound **1**, which is expected to exhibit a new type of valence tautomerism *via* an S_N2 transition state of a highly symmetrical nature as shown in Fig. 1. We report here structural and NMR studies of this unique sulphur compound.

The key reaction in the synthesis[†] is the cyclization of a dithiocarbamato group[7] in tris(*N,N*-dimethyldithiocarbamato)methane **3**, which was obtained from the corresponding known bis(*N,N*-dimethyldithiocarbamato)methane **2**,[8] as shown in Scheme 1.

Fig. 2 shows the molecular structure determined by X-ray crystal analysis of the dithiocarbamate dimer cation.[‡] One of the dithiocarbamato groups forms a 1,3-dithietane ring

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[†] *Syntheses*: To 75.35 g of the known compound **2** in 1.5 l of anhydrous tetrahydrofuran was added dropwise 191 ml of a 1.55 mol dm^{-3} hexane solution of butyllithium while maintaining the temperature at −50 °C. To the resulting bright-yellow solution was added solid tetramethylthiuram disulphide (71.32 g), at once, at −50 °C. When the reaction mixture was allowed to warm slowly with stirring overnight, the crystalline product (77.3 g) **3** precipitated. M.p., 205 °C (decomp.). To 4.0 g of **3** was added methyl iodide (*ca.* 40 ml) until complete dissolution occurred. When the resulting solution was allowed to stand in the dark overnight, light-yellow crystals of **1a** were obtained. This crude iodide was dissolved in warm ethanol (500 ml), and to the solution was added sodium tetraphenylborate (3 g) dissolved in a small amount of ethanol. After cooling, 4.4 g of the tetraphenylborate **1b** was obtained. It was recrystallized from boiling acetone. M.p., 156 °C (decomp.). NMR (60 MHz, [$^2H_3$]acetonitrile): δ 3.19 (s, 6, N^+–CH_3), 3.30 (s, 3, N–CH_3), 3.42 (s, 3, N–CH_3), 5.42 (s, 1, CHS_3) and 6.55–7.21 (m, 20, Ph H).

[‡] *Crystal data* for $C_{31}H_{33}BN_2S_4$: M_W = 572.69; triclinic, space group, $P\bar{1}$; a = 9.616(2), b = 10.568(2), c = 15.176(3) Å, α = 78.33(2), β = 80.36(2), γ = 87.89(2)°; V = 1489.1 Å^3; z = 2; D_c = 1.28 g cm^{-3}; $F(000)$ = 604; monochromated Mo-Kα, λ = 0.71073 Å; μ = 3.3 cm^{-1}; crystal size, 0.25 × 0.45 × 0.28 mm; 5621 reflections (maximum 2θ = 50°) were collected with a Syntex-Nicolet $P2_1$ diffractometer and 5277 reflections were unique. The structure was solved by direct methods. The refinement was performed by full-matrix least-squares analysis using 3664 reflections with $F_o^2 > 3.0\sigma(F_o^2)$. After anisotropic refinement a majority of the hydrogens including H(4) were clearly visible in the difference map. The hydrogens were placed at idealized positions and were included in the refinements with fixed thermal parameters and their coordinates 'riding' on the carbon to which they are bonded. The final cycle of refinement converged with unweighted and weighted agreement factors of 0.041 and 0.052, respectively. All calculations were performed on a VAX computer using a SDP/VAX program. In the counteranion, the boron atom has a slightly distorted tetrahedral coordination with C–B–C angles in the range of 103–113°. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

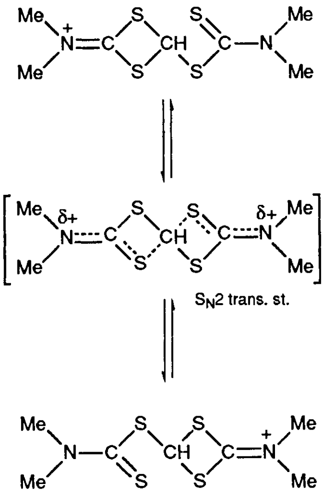
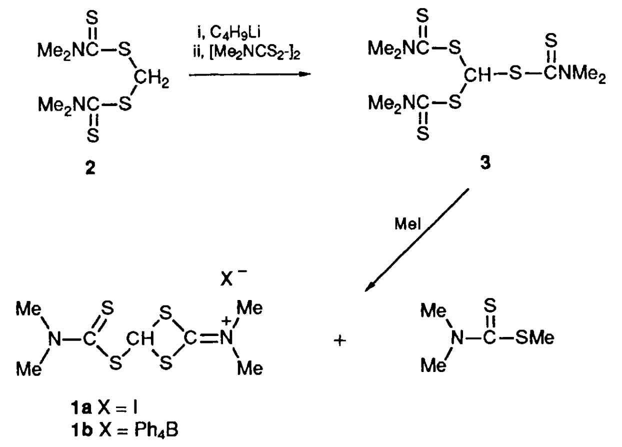


Fig. 1 Possible valence tautomerism of dithietane **1**



Scheme 1

together with the central carbon atom C(4). The formation of the dithietane ring results in a highly distorted tetrahedron around the central C(4) atom. An important structural feature is the presence of the close contacts of S(4)–C(4) (2.941 Å) and S(4)–S(1) (2.981 Å). These distances are significantly shorter than the values predicted for the corresponding van der Waals contacts (S–C, 3.55; S–S, 3.70 Å): the sulphur van der Waals radius is 1.85 Å and the half-thickness of an aromatic ring (corresponding to the carbon van der Waals radius) is 1.70 Å.[9] The close C(4)–S(4) contact shows the formation of an incipient bond between these atoms and suggests the occurrence of the ring-opening/ring-closing tautomerism that is shown in Fig. 1. The ^{1}H NMR spectra in acetonitrile solution provide additional evidence for this valence tautomerism.[10] Fig. 3 shows the NMR spectra of the *N*-methyl protons at different temperatures. The spectrum at 25 °C exhibited three *N*-metyl proton peaks: two at δ 3.42 (s, 3) and 3.30 (s, 3) attributed to the two nonequivalent dithiocarbamato methyl groups and the other at δ 3.19 (s, 6) of the iminium methyl substituents. Upon heating, the three individual peaks broadened and their maxima moved closer together; at >65 °C, a single peak was observed. After cooling, the room temperature spectrum was reproduced. From the NMR spectra observed at <45 °C, two results were obtained: (*i*) the separation of the two dithiocarbamato methyl proton peaks was temperature independent, and (*ii*) the midpoint of these peaks moved closer to the iminium

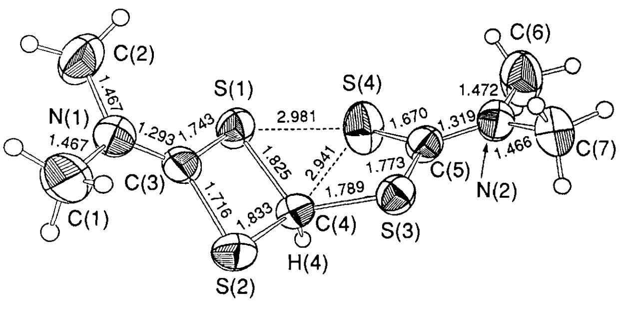


Fig. 2 Molecular structure of $[Me_2NCS_2{\cdot}CH{\cdot}S_2CNMe_2]^+$. Two dithiocarbamato groups are linked by the central carbon atom C(4), which is bonded to one hydrogen atom H(4) and three sulphur atoms, S(1), S(2) and S(3), from the two dithiocarbamates. The C, N and S atoms of each dithiocarbamato group form a plane together with C(4), and the molecular planes of the two groups make a dihedral angle of 118.5° at C(4). The bond angles around the C(4) atom are: S(1)–C(4)–S(2) 95.2°, S(1)–C(4)–S(3) 115.1°, S(1)–C(4)–H(4) 114.6°, S(2)–C(4)–S(3) 108.8°, S(2)–C(4)–H(4) 120.9°, S(3)–C(4)–H(4) 102.8°.

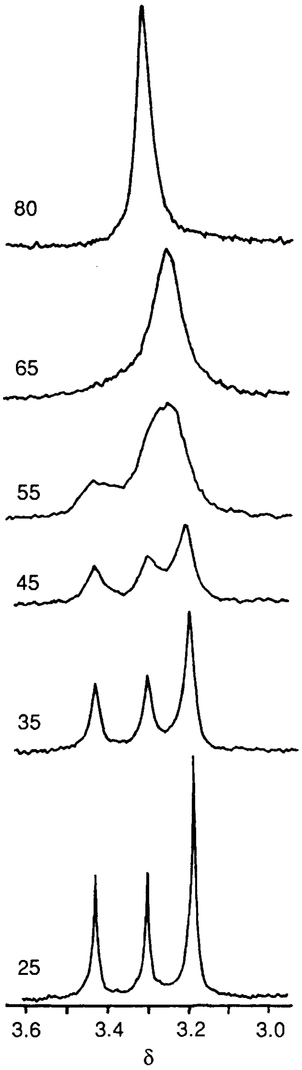


Fig. 3 *N*-methyl ^{1}H NMR spectra observed for $[Me_2NCS_2{\cdot}CH{\cdot}S_2CNMe_2]^+$ in CD_3CN at 200 MHz at different temperatures

methyl proton peak. The first result shows that an internal rotation about the C–N bond has a much lower rate than the NMR time-scale. Therefore, the temperature dependence of the N-methyl proton signals can be explained by the interconversion between the two equivalent structures of Fig. 1. The energy barrier of this equilibrium was calculated to be approximately 5 kcal mol^{-1} (1 cal = 4.184 J), which is much smaller than the values (15.9–17.1 kcal mol^{-1}) reported for the barriers of internal rotation about the C–N bond in dimethyldithiocarbamic acid esters.[11]

The present NMR study has detected the degenerate rearrangement of Fig. 1 in solution. The X-ray crystal analysis has shown that the molecular structure in the solid state is favourably oriented for the rearrangement in solution.

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