Stereochemical Consequences of Transannular S–Cl · · · S Interactions in Sulphur Nitrogen Chemistry; Preparation and Structure of $[(Me_2N)_2C_2N_4S_2Cl]^+[Cl_3]^-$

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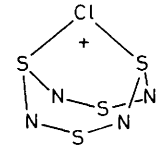
The oxidation of 3,7-bis(dimethylamino)-1,5-dithia-2,4,6,8-tetrazocine yields the *S*-chloro salt $[(Me_2N)_2C_2N_4S_2Cl]^+[Cl_3]^-$, whose crystal and molecular structure has been determined by *X*-ray crystallography; the molecular structure of the cation and the cation–anion contacts are related to the stereochemistry of chlorination of transannular sulphur–sulphur interactions in cyclothiazenes.

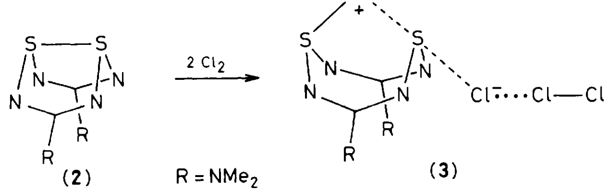
Recently we suggested that the ligand orientations exhibited by $S_4N_4X_2$ compounds could be rationalized in terms of the dominant frontier orbital interactions between S_4N_4 and an approaching oxidant.[1] Thus the *endo–exo* geometry of $S_4N_4Cl_2$[2] was depicted as arising from the preliminary electrophilic attack of Cl^+ on the high-lying S–S bonding orbital ($4b_2$) of S_4N_4. However, while the existence of bridged chloronium ions is well established in organic chemistry,[3] there is no direct evidence for intramolecularly bridged species in sulphur nitrogen chemistry. Indeed the structure of $[S_4N_4Cl]^+[FeCl_4]^-$ provides little support for the idea.[4] The characterization of intermediates which support the viability of the putative transition state (**1**) is therefore of primary importance to future mechanistic discussions. To this end we are exploring the stereochemistry of chlorination of model compounds related to S_4N_4. We report herein that the chlorination of 3,7-bis(dimethylamino)-1,5-dithia-2,4,6,8-tetrazocine (**2**)[5] yields the ionic compound $[(Me_2N)_2C_2N_4S_2Cl]^+[Cl_3]^-$ (**3**). *X*-Ray crystallographic analysis of (**3**)† reveals a puckered $C_2N_4S_2$ cation possessing an asymmetric S–Cl · · · S transannular bridge.

The title compound can be prepared by passing chlorine gas over a saturated solution of (**2**) in acetonitrile. Cooling the resulting solution to −30 °C yields orange, moisture sensitive crystals of (**3**), decomp. 97—100 °C. An ORTEP drawing of the cation and anion in (**3**) is shown in Figure 1. The eight-membered $C_2N_4S_2$ ring is bisected by a crystallographic mirror plane containing both sulphur atoms. The trichloride anion also lies in this plane. The dihedral angle between the mean planes of the two CN_2S_2 units (126°) in the cation is larger than in compound (**2**) (101°), and the S · · · S contact (3.491 Å) has opened up considerably [from 2.428 Å in (**2**)]. The S–N bonds to S(1) (1.542 Å) and S(2) (1.514 Å) are markedly shorter than in (**2**) (mean 1.605 Å), while the C(1)–N(1) (1.363 Å) and C(1)–N(2) (1.366 Å) bonds remain virtually unchanged [mean C–N distance in (**2**) 1.348 Å]. In accord with our mechanistic predictions the chlorine atom Cl(1) straddles the two sulphur atoms, but the S–Cl · · · S unit is noticeably asymmetric. Nonetheless the primary S(1)–Cl(1) distance (2.290 Å) is significantly longer than the S–Cl bonds in $S_4N_4Cl_2$ (*endo* 2.179, *exo* 2.183 Å)[2a] and $[S_4N_4Cl]^+[FeCl_4]^-$ (2.139 Å),[4] while the secondary S(2) · · · Cl(1) contact (3.225 Å) is much shorter (3.501 and 3.448 Å in $[S_4N_4Cl]^+[FeCl_4]^-$ and $S_4N_4Cl_2$, respectively). The mean of S(2)–C(1) and S(1) · · · Cl(1) (2.758 Å) is shorter than the intermolecular S · · · Cl · · · S distance in S_4N_5Cl (2.811 Å).[6]

The 400 MHz ^1H n.m.r. spectrum of (**3**) in $CDCl_3$ at −90 °C shows a sharp singlet for the NMe_2 protons at δ 3.34. The



(1)



(2) (3)

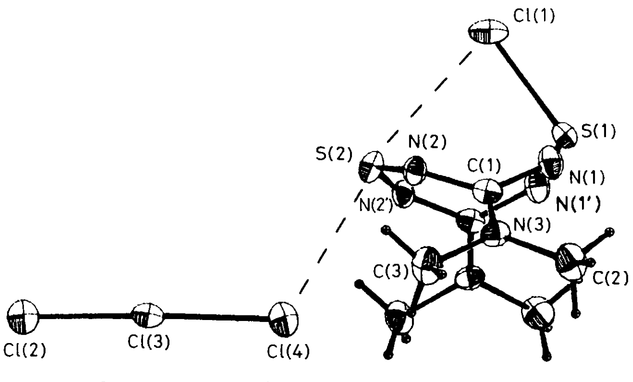


Figure 1. ORTEP drawing (30% probability ellipsoids) of a cation–anion pair in $[(Me_2N)_2C_2N_4S_2Cl]^+[Cl_3]^-$. Selected bond lengths (in Å) and bond angles (in °) are: S(1)–Cl(1) 2.290(3), S(1)–N(1) 1.542(6), N(1)–C(1) 1.363(7), N(2)–C(1) 1.366(7), N(3)–C(1) 1.277(7), N(3)–C(2) 1.501(7), N(3)–C(3) 1.487(8), S(2)–N(2) 1.514(5), S(2) · · · Cl(1) 3.225(4), S(2) · · · Cl(4) 3.160(4), Cl(4)–Cl(3) 2.393(4), Cl(3)–Cl(2) 2.183(4); N(1)–S(1)–N(1') 117.5(4), S(1)–N(1)–C(1) 131.0(5), N(1)–C(1)–N(2) 124.1(4), C(1)–N(2)–S(2) 135.0(4), N(2)–S(2)–N(2') 123.3(4), Cl(4)–Cl(3)–Cl(2) 177.7(2).

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† *Crystal data*: $C_6H_{12}N_4S_2Cl_4$, M = 374.1, orthorhombic, space group *Pnma*, a = 23.644(3), b = 10.773(3), c = 5.862(2) Å, Z = 4, U = 1493.1 Å^3, D_c = 1.664 g cm^{-3}. Data were collected on an Enraf-Nonius CAD-4 automated diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) using ω—2θ scans ($\theta_{max.}$ of 25°), and were corrected for absorption. The structure was solved by direct methods and refined by full-matrix least-squares to an R-value of 0.091 for 750 observations ($F > 6\sigma_F$) and 91 parameters (H-atom positions were determined from difference Fourier map information and idealization; their positions were not refined). Attempts to refine the structure in the acentric space group corresponding to *Pnma* led to unrealistic bond lengths. The atom co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

equivalence of the two methyl resonances at this temperature suggests either a rapid rotation of the NMe_2 groups about the respective C–N bonds or, more likely, a rapid exchange of the bridging chlorine between the two sulphur atoms, *i.e.* a symmetric structure on the n.m.r. time scale. The asymmetry of the S–Cl · · · S unit in the solid state can be related to the effects of secondary bonding to the anion. The Cl_3^- ion lies under the fold of the $C_2N_4S_2$ ring opposite the bridging Cl(1) atom (see Figure 1). The Cl_3 unit is almost linear [Cl(4)–Cl(3)–Cl(2) 177.7°], but markedly asymmetric [Cl(4)–Cl(3) 2.393, Cl(3)–Cl(2) 2.183 Å], with the more loosely bonded atom Cl(4) approaching closely (3.160 Å) the S(2) from a direction approximately *trans* [Cl(1)–S(2)–Cl(4) 169.1°] to the bridging Cl(1) atom. Such an arrangement is consistent with the onset of the expected frontier orbital interaction between the cation–anion pair; it illustrates the incipient nucleophilic attack of the π^* HOMO of Cl_3^- (a 'solvated' chloride ion)[3] on the S · · · Cl antibonding LUMO of the bridged cation.[7] The importance of the transannular S · · · Cl interaction in guiding the approach of the incoming nucleophile to the *exo*-position is thus clearly demonstrated.

The isolation of (**3**) as a stable cation–anion pair rather than a covalent dichloride, as in $S_4N_4Cl_2$, may reflect the smaller size of the $C_2N_4S_2$ (*vs.* S_4N_4) ring, which would bring the two sulphur atoms together, and facilitate the transannular S–Cl · · · S interaction. There may also be an electronic influence exerted by the dimethylamino groups in stabilizing the charge on the cation.

We thank the Natural Sciences and Engineering Research Council of Canada, the National Science Foundation, and State of Arkansas for financial support.

Received, 28th January 1985; Com. 126

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