Crystal and Molecular Structure of *SS*-Diethyl-*N*-dichloroacetylsulphilimine

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Summary The structure of $Et_2S:N\,CO\,CHCl_2$ has been determined by *X*-ray analysis and its electronic structure and conformation are discussed

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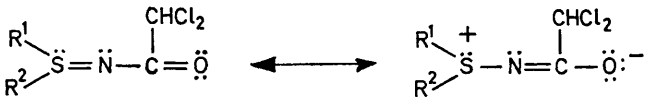
Previously[1] it was assumed that the resonance (Ia) ↔ (Ib) is characteristic of *N*-halogenoacetylsulphilimines and that


(Ia) (Ib)

the S^{IV}–N $d\pi$ bond is somewhat weaker than that in *N*-sulphonylsulphilimines. These conclusions are verified by the present *X*-ray structure determination of $Et_2S{\cdot}N{\cdot}CO{\cdot}CHCl_2$; *cf.* the SN, CN, and CO bond lengths in Figure 1 and the planarity of the S,N,C(2),O,C(1) moiety.

Crystal data Colourless, mostly twinned crystals of $C_6H_{11}ONSCl_2$ (M 216·14) are monoclinic, space group $P2_1/n$ (No. 14) with $a = 6{\cdot}946(6)$, $b = 11{\cdot}323(6)$, $c = 12{\cdot}450(10)$ Å, $\beta = 95{\cdot}29(9)°$, $U = 975{\cdot}0$ Å^3, $D_c = 1{\cdot}472$, $D_0 = 1{\cdot}468$ g cm^{-3}, $Z = 4$, $F(000) = 448$, and $\mu(\text{Cu-}K_\alpha) = 74{\cdot}7$ cm^{-1}.

The intensities of 963 independent reflections were recorded on integrated Weissenberg photographs.† The structure was solved by symbolic addition and Fourier methods. Least-squares refinement (using anisotropic thermal parameters for the non-hydrogen atoms) has reached an R factor of 0·103.

The S–N bond length determined is different from that of 1·692 Å calculated[3] from i.r. data. Similarly to *N*-sulphonylsulphilimines, S^{IV}–C; distances differ significantly in $Et_2S{:}N{\cdot}CO{\cdot}CHCl_2$ (Figure 1). The bond angles in the S(C,C,N) pyramid are similar to the corresponding ones in *N*-sulphoxylsulphilimines and to the S(C,C,O) angles of sulphoxides, indicating the same hybridization of the S^{IV} atom in all these compounds. The rather low C(2)–N–S^{IV} bond angle can be explained by the repulsion effect of the lone pair of the sp^2 nitrogen atom.

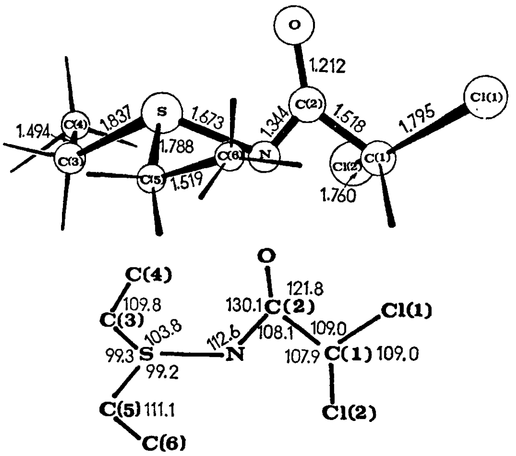


FIGURE 1. *Conformation, bond lengths, and bond angles of crystalline* SS-*diethyl*-N-*dichloroacetylsulphilimine.*

The dichloroacetyl group is linked asymmetrically to the nitrogen atom of the Et_2SN group (Figures 1 and 2; *cf.* asymmetric conformation of the *S*-symmetric *N*-sulphonylsulphilimines[2]). It is characteristic of the arrangement around the C(2)N group that the carbonyl oxygen and the lone pair of the nitrogen atom are *trans*, owing to repulsion. The relatively large value of the N–C(2)–O bond angle (130·1°) may be explained by the *cis* arrangement of the sulphur and oxygen atoms and by the repulsion between the C(2)–N and C(2)–O π-bonds.

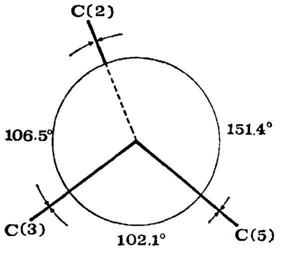


FIGURE 2. *Newman projection of the* (C,C)S–N(C) *group in* $Et_2S{:}N{\cdot}CO{\cdot}CHCl_2$.

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† Crystals (A. Kálmán and G. Argay, *J. Sci. Instr.*, 1965, **42**, 483; A. Kálmán, *ibid.*, 1967, **44**, 643.) were changed after each layer in order to diminish the errors caused by decomposition during exposures.

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