Structure of the Compound Purported to be *NN*-Bis(chloromethyldimethylsilyl)-acetamide: *X*-Ray Crystal Structure Analysis of the Novel Five-membered Oxygen-, Silicon-, and Nitrogen-containing Heterocycle (*O–Si*)-Chloro-[(*N*-chlorodimethylsilylacetamido)methyl]dimethylsilane

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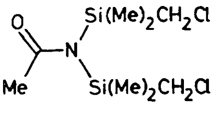
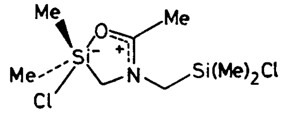
Summary The compound erroneously reported as *NN*-bis(chloromethyldimethylsilyl)acetamide has been proven by single-crystal *X*-ray analysis to be (*O–Si*)-chloro-[(*N*-chlorodimethylsilylacetamido)methyl]dimethylsilane.

Trans-silylation of bis(trimethylsilyl)acetamide (BSA) with chloromethyldimethylchlorosilane results in a solid product which has been reported to have the *NN*-disilylamide structure (I).[1] The ^{1}H n.m.r. spectrum (C_6H_6) of this product contains two singlets for the $SiMe_2$ groups [δ 0·08 (6H) and 0·96 (6H)], a barely resolved quartet for the $SiCH_2$ groups [δ 2·45 (2H) and 2·77 (2H)], and a barely resolved triplet for the COMe group [δ 1·41 (3H)]. The ^{1}H n.m.r. spectrum of the corresponding ^{15}N isotopomer, prepared from [^{15}N]BSA, is identical to that of the ^{14}N derivative except that the upfield $SiCH_2$ resonance appears as a doublet (J 1·9 Hz) and the COMe resonance is a broad multiplet. Whereas these spectra are temperature invariant from −60 to *ca.* 120 °C, above 120 °C the SiMe resonances broaden and by 140 °C they have coalesced to a very broad peak. The i.r. spectrum of the ^{14}N isotopomer contains a number of absorptions which differ by > 5 cm^{-1} from those of the ^{15}N derivative [^{14}N(^{15}N), CCl_4, cm^{-1}]: 1589 (1580) s, 1514 (1500) m, 1229 (1219) m, 1168 (1153) w, and 1050 (1042) w. Molecular weight measurements in C_6H_6 reveal that the compound is monomeric in dilute solution but is somewhat associated at higher concentrations (M_{calc} = 272; at 0·1M M_{obs} = 369).



(I)



(II)

The fact that ^{15}N–^{1}H coupling is observed for only one of the $SiCH_2$ groups, the high coalescence temperature, and the effect of isotopic substitution on the i.r. spectrum are all incompatible with the reported amide structure (I).[†] In

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[†] For *NN*-bis(trimethylsilyl)formamide the coalescence temperature is −46 °C and the intense absorption at 1659 cm^{-1} does not shift upon substitution of ^{15}N (C. H. Yoder, W. C. Copenhafer, and B. DuBeshter, *J. Amer. Chem. Soc.*, 1974, **96**, 4283).

order to determine the constitution of the product unequivocally a single crystal was sealed inside a thin-walled glass capillary and subjected to *X*-ray analysis. Crystals belong to the triclinic system, space group $P\bar{1}$, $a = 12{\cdot}331(5)$, $b = 11{\cdot}279(5)$, $c = 8{\cdot}032(4)$ Å, $\alpha = 92{\cdot}02(3)$, $\beta = 100{\cdot}59(3)$, $\gamma = 106{\cdot}78(3)°$, $Z = 2$. The structure was solved by direct methods using MULTAN.[2] Full-matrix least-squares refinement of atomic positional and thermal (anisotropic C, Cl, N, O, Si; isotropic H) parameters converged to R 0·049 over 1863 statistically significant [$I > 2{\cdot}0\sigma(I)$] reflections.‡ The results of the *X*-ray analysis establish that the product has structure (II) in which the geometry at the five-co-ordinate silicon atom is distorted trigonal bipyramidal with the chlorine and oxygen atoms occupying axial sites; the molecular conformation is illustrated in the Figure. The planar conformation (maximum deviation 0·007 Å) of the heterocyclic ring and the intermediate nature of the C–O and C–N bond lengths indicate that the structure is best represented as shown in (II) rather than as either of the two extreme forms containing C=O or C=N ring bonds. The compound, unusual in that it was formed by substitution at the chloromethylene group rather than at the silicon atom, is also novel in other respects. It is one of the few examples wherein five-co-ordination at silicon results from intramolecular dative bonding, and its isolation yields a stable representative of the five co-ordinate type of structure which has been postulated as being involved in a variety of silyl group migration reactions.[3]

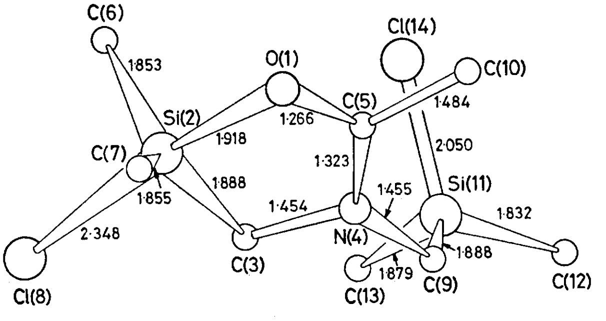

FIGURE. Molecular conformation, atom numbering scheme, and bond lengths (Å) (σ range 0·002—0·006 Å); hydrogen atoms have been omitted for clarity.

The structure (II) derived from the *X*-ray analysis provides a ready explanation for the high coalescence temperature and the effect of isotopic substitution on the i.r. spectrum (*e.g.* probable coupling of the N$\cdots$C and C$\cdots$O vibrations resulting in shifts for the absorptions at 1514 and 1549 cm^{-1}). The differences in the magnitude of the ^{15}N couplings to the methylene protons are consistent with their stereospecific character and the averaging that occurs at the four-co-ordinate silicon owing to rotational motion of the $ClSiMe_2CH_2$ group in solution.[4] The association in benzene at higher concentrations parallels that found for silatranes, which also contain a five-co-ordinate silicon atom.[5]

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‡ The atomic 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.

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