

Absolute Configuration of a Chiral *N*-Chloroaziridine with Molecular Asymmetry due solely to a Trivalent Nitrogen Atom. X-Ray Structure of (*R*)-(–)-1-Chloro-2,2-diphenylaziridine

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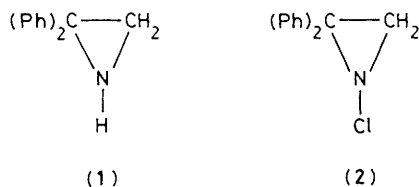
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X-Ray analysis of the crystalline optically active 1-chloro-2,2-diphenylaziridine, obtained by chlorination of 2,2-diphenylaziridine with *t*-butyl hypochlorite in the presence of a chiral trifluoro-alcohol, followed by fractional crystallization of the crude reaction product, shows that the absolute configuration at the chiral nitrogen atom of the derivative is (–)-(*R*).

Recently, we observed that chlorination at the nitrogen atom of 2,2-diphenylaziridine (**1**) with achiral *t*-butyl hypochlorite (Bu^tOCl), when carried out in the presence of chiral trifluoro-alcohols, affords partially optically active 1-chloro-2,2-diphenylaziridine (**2**).¹ This compound exists in a relatively stable crystalline form, and we now report that its optical purity may be enhanced simply by fractional crystallization of the asymmetric crude reaction product.

Fractional crystallization from diethyl ether–light petroleum (40–60 °C) of a sample of (**2**) $\{[\alpha]_D^{20} -95.63^\circ (\text{CHCl}_3)\}$, obtained by chlorination of (**1**) with Bu^tOCl at –60 °C in the presence of (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol, afforded the *N*-chloro derivative with m.p. 26–30 °C and $[\alpha]_D^{20} -283.7^\circ (\text{CHCl}_3)$. The ¹H n.m.r. spectrum of this derivative, recorded in the presence of the chiral shift reagent tris[3-(heptafluoropropyl)hydroxymethylene]-(+)-camphora-



to]europium(III)[(+)-Eu(hfc)₃], suggests that its enantiomeric purity is not less than 85%.

The crystalline properties and the presence of the chlorine atom in compound (2), prompted us to study the molecular structure and the absolute configuration at the chiral nitrogen atom of the (-)-(2) enantiomer, by means of an X-ray diffraction analysis, taking into account the effect of anomalous dispersion. This analysis was carried out on a crystal of 0.2 × 0.2 × 0.3 mm selected from the enantiomerically enriched (-)-(2) sample described above. The optical activity, checked immediately after the X-ray measurements, showed the same negative sign. To the best of our knowledge, this is the first example of an X-ray crystal structure determination of the absolute configuration at a chiral compound having the tetravalent nitrogen atom as the sole asymmetric centre.

Crystal data: C₁₄H₁₂NCl, *M* = 229.7, monoclinic, space group *P*2₁, *a* = 21.3705(8), *b* = 8.9867(2), *c* = 13.5224(7) Å, β = 108.40(1)°, *Z* = 8, *D*_c = 1.238 g cm⁻³, *U* = 2464.1 Å³, Cu-*K*_α radiation, λ = 1.5418 Å. 3681 Independent reflections were collected in the range 4° ≤ θ ≤ 58°, while 1729 Friedel opposites were collected in the range 10° ≤ θ ≤ 42° with a θ-2θ scan using a scan width of 1.3° and a speed of 0.05° s⁻¹. During data collection the intensities of two reference reflections, monitored every 100 reflections, decreased to 85% of their original value. The data were scaled accordingly. Semi-empirical absorption corrections were made on the basis of φ-scan data with three different 2θ values. The structure was solved by direct methods and refined by blocked full-matrix least-squares to a conventional *R* factor of 0.071. There are four molecules in the asymmetric unit and in Figure 1 we give the numbering scheme and the relevant bond lengths averaged over the four molecules. The absolute configuration of the

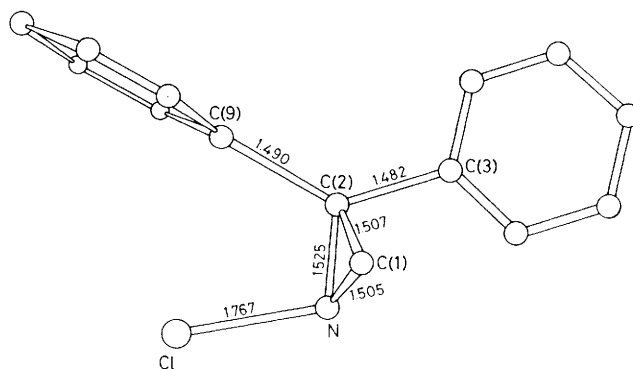


Figure 1. X-Ray structure of (-)-1-chloro-2,2-diphenylaziridine. Arbitrary view of one of the four independent molecules. Bond lengths (Å) are averaged over equivalent observables.

title compound was determined by selecting the 316 Friedel opposites which showed a Bijvoet ratio greater than 0.04 and by making use of these most enantiomer-sensitive reflections in a structure factor calculation to discriminate between the two enantiomers. The (*R*)-model gave a conventional *R* factor of 0.064 (*R*_g = 0.095) while the (*S*)-model gave an *R* factor of 0.088 (*R*_g = 0.121).†

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References

- 1 A. Forni, I. Moretti, A. V. Prosyaniuk, and G. Torre, *J. Chem. Soc., Chem. Commun.*, 1981, 588.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.