The Crystal Structure of the Hemihydrochloride of Coccinellin, the Defensive *N*-Oxide Alkaloid of the Beetle *Coccinella Septempunctata*, a Case of Symmetrical Hydrogen Bonding

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Summary The structure of the hemihydrochloride of the defensive *N*-oxide alkaloid of the ladybird, coccinellin, $C_{13}H_{23}NO$, has been determined by single-crystal *X*-ray diffraction; two molecules are linked together through their oxygen atom *via* a symmetrical hydrogen bond, the O–O distance being 2·43 Å.

This analysis of coccinellin is the first complete structure determination in the course of a study of a series of ladybird alkaloids.[1] Coccinellin is unusual in that it is synthesised by the insect.[1b] The previous study[1] of coccinellin with n.m.r. and m.s. (using ^{13}C n.m.r.), has shown that the molecule has a mirror plane and suggested two possible structural formulae. Our *X*-ray analysis has shown one of them to be correct. The molecule having *cis*-configuration is depicted in the figure.

Crystal data: thin transparent regular plates, $(C_{13}H_{23}NO)_2$,-HCl; $M = 455{\cdot}13$; monoclinic space group $A2/m$; $a = 13{\cdot}239(3)$, $b = 9{\cdot}162(2)$, $c = 12{\cdot}241(2)$ Å, $\beta = 121{\cdot}57(1)°$; $U = 1265$ Å^3; $D_m = 1{\cdot}181$ g cm^{-3} (flotation in CCl_4 and cyclohexane), $D_c = 1{\cdot}194$ g cm^{-3}; $Z = 2$.

The cell parameters were refined from data collected on a Hilger-Watts four-circle diffractometer, controlled by a PDP-8 computer. Data collected with the diffractometer using Mo-K_α radiation were reduced to 499 independent reflections and corrected for the Lp-factor but not for absorption. The structure was solved by direct methods using the MULTAN program.[2] Difference Fourier maps clearly revealed all hydrogen atoms. The structure was refined anisotropically, keeping the hydrogen atoms fixed, by the full-matrix least-squares method, to an *R*-factor of 0·06, using all 499 reflections with unit weight. The chloride ion was found to be disordered, and distributed at two different special positions, (0·5, 0·064, 0·0) and (0·474,

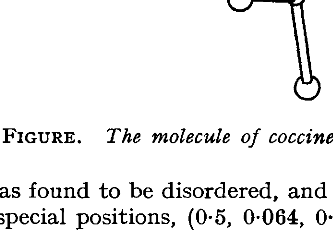

FIGURE. *The molecule of coccinellin.*

0·0, −0·058) with a refined occupancy of 0·229(4) and 0·031(3), respectively.

The cation is dimeric and consists of two molecules linked together *via* a symmetrical hydrogen bond between the oxygen atoms of the NO groups, the hydrogen atom lying in the origin. The O–H distance is 1·214(7) Å and the N–O–H angle is 109·5(4)°.

I.r. studies[3] have indicated the presence of symmetrical hydrogen bonding in the solid state of pyridine 1-oxide and 2-picoline 1-oxide 2:1 adducts with HCl and HBr. Symmetrical hydrogen bonds have also been found in the cation of di(acetamide) monochloride[4] and in anionic species as alkali-hydrogen biscarboxylates[5] with oxygen–oxygen distances *ca.* 2·44 Å. The N–O distance of 1·425(7) Å compares with that found in trimethylamine oxide hydrochloride.[6] The N–O distance in the free base is shorter, 1·39(1) Å.[7]

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