complex was treated with anhydrous HCl to give *trans*-chloro-*p*-fluorophenylbis(triethylphosphine)platinum(II), m.p. 103–104°. The other halogen and pseudohalogen complexes (**2**: X = Br, I, SCN, and CN) were prepared by simple metathetical reactions of the chloro compound. The aryl and methyl compounds (**2**: X = C_6H_5, *m*-FC_6H_4, and CH_3) were obtained by reaction of the appropriate Grignard reagents with the chloride. The *m*-fluorophenylplatinum compounds were prepared by similar procedures. The *trans* configurations of all the compounds studied were confirmed by the proton magnetic resonance technique of Jenkins and Shaw.[7] The CH_3 resonance of the triethylphosphine ligands appeared as a characteristic five-line structure (J = 7.8 ± 0.3 c.p.s.) owing to coupling with the CH_2 protons and with the two *trans* P^{31} nuclei equivalently.

(7) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

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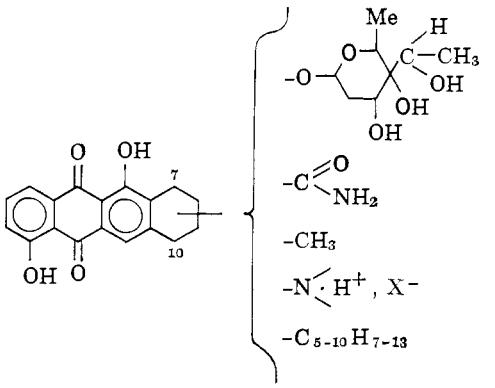
RECEIVED OCTOBER 13, 1964

The Structure of Isoquinocycline A. An X-Ray Crystallographic Determination[1]

Sir:

Recently, a partial structure has been proposed for isoquinocycline A based on spectroscopic, degradative, and chemical studies.[2] Two major and several minor features of the antibiotic have been established or suggested. These results are summarized as follows



This communication presents the complete structure of the molecule and its relative stereochemistry as determined by the X-ray method.[3]

A satisfactory partial structure for the antibiotic was obtained through the use of the weighted isomorphous replacement method.[4] In this way, it was demonstrated that structures can be solved in the *noncentrosymmetrical* case employing isomorphous replacement procedures with the information that is available from only *two* isomorphous derivatives (the hydrochloride and the hydrobromide in the present example).[5] The partial structure (22 atoms plus bromine) was then augmented, in steps, using more conventional techniques until 58 atoms (excluding hydrogen) were finally fixed.

The two salts, crystallized from dioxane–water, were found to be orthorhombic, with space group $P2_12_12_1$, and their cell dimensions agreed within 0.2–0.3%. The density of the hydrobromide gave an X-ray molecular weight of 886 which, from elemental analysis, placed the asymmetric unit at $C_{40-41}H_{47-53}N_2O_{13-14}Br$. Considering the empirical formula favored for the antibiotic,[2] the high carbon and oxygen content suggested that dioxane and possibly water of solvation were present in the crystals.

The positions of the chloride and bromide ions were determined from three principal difference Patterson projections employing coefficients of the type $(|F|_{Br} - |F|_{Cl})^2$, where $|F|_{Br}$ and $|F|_{Cl}$ are the structure amplitudes of the hydrobromide and hydrochloride salts, respectively. Their x-coordinate proved to be special ($x \sim 0$) and, consequently, generated an unwanted mirror plane of symmetry at $x = 1/2$ in the weighted electron density. The relative and absolute scales of the two isomorphs, requisite to the weighted isomorphous replacement method, were first obtained by Wilson's method and then verified and improved upon from two-dimensional structure factor and electron density considerations. The zero contribution of the replaceable electrons to certain classes of two-dimensional reflections and a comparison of peak heights (excluding bromide and chloride) in projected electron densities served to obtain a self-consistent relative scale which was then fixed on an absolute basis by comparing the observed projected peak heights and peak shapes of the ions with those based on computation, systematically varying an isotropic thermal parameter for the ions. The weights for the observed structure amplitudes, functions of $|F|_{Br}$, $|F|_{Cl}$, and the replacable electron contribution, were computed but they proved to be, in general, inapplicable in a direct manner. A very large number of them had an absolute value greater than unity and these usually ranged between ±10. Such behavior was assumed to be the result of observational errors in intensity so their effect on the weight computation was assessed by approximating the standard error of the weight in terms of the estimated standard error of the structure amplitudes. Then, somewhat arbitrary but rather stringent criteria were employed to select acceptable weights. These were used to compute a weighted electron density. The density contained 146 peaks greater than 1 eÅ.$^{-3}$ in the asymmetric unit, of which about 73 were related by mirror symmetry. A 22-atom partial structure (the tetracyclic nucleus and its hydroxyl and carbonyl substituents) was easily derived and it served as a starting point for the use of more conventional methods to obtain the remainder of the structure.

The structure of isoquinocycline A is shown above, from which most of the stereochemistry is self-evident. The antibiotic consists of five fused rings joined to a pyrrolopyrrole *via* a spiro atom and also to a sugar-like

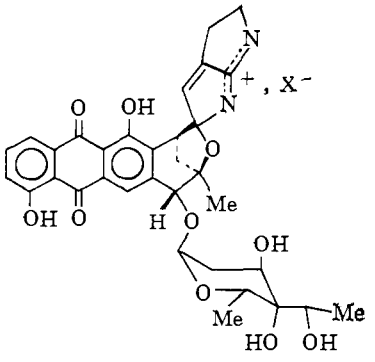
(1) This research has been supported by the National Institutes of Health, U. S. Public Health Service, and Lederle Laboratories Division, American Cyanamid Co.

(2) D. B. Cosulich, J. H. Mowat, R. W. Broschard, J. B. Patrick, and W. E. Meyer, *Tetrahedron Letters*, **No. 7**, 453 (1963); *ibid.*, **No. 13**, 750 (1964).

(3) A preliminary account of this work was presented at the Annual American Crystallographic Association Meeting held in March, 1963, at the Massachusetts Institute of Technology, Cambridge, Mass.

(4) G. Kartha, *Acta Cryst.*, **14**, 680 (1961).

(5) The author wishes to thank the Organic Chemical Research Section, Lederle Laboratories Division, American Cyanamid Co., for supplying these samples.



$C_{33}H_{32}N_2O_{10}\cdot HX$

moiety through a glycosidic link, with the pyrrolopyrrole nitrogen atoms away from the aromatic nucleus and the furan-pyrrolopyrrole system *trans* to the sugar.

The pyrrolopyrrole is planar within ±0.04 Å. and contains one carbon–carbon double bond. Both nitrogen-to-bridge-carbon distances are equal and shorter than expected for a carbon–nitrogen single bond (1.33 and 1.31 ± 0.03 Å.). The two secondary hydroxyl groups of the sugar are hydrogen bonded with dioxane molecules of solvation. The latter occupy relatively large cavities in the solid between antibiotic molecules and probably assist in maintaining the orientation of the sugar moiety.

The details of this structure determination will be submitted to *Acta Crystallographica*.

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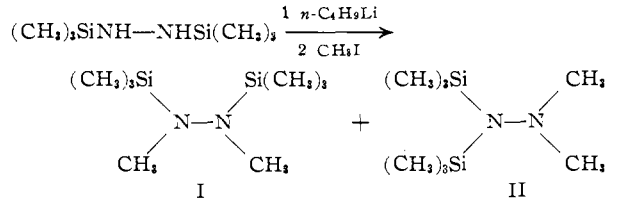
RECEIVED OCTOBER 15, 1964

A Novel Rearrangement of 1,2-Bis(trimethylsilyl)hydrazine

Sir:

In extending the work of Wannagat and co-workers on organosilylhydrazines,[1] we have found a novel rearrangement involving migration of silicon from one nitrogen atom to another. If 1,2-bis(trimethylsilyl)-hydrazine is treated with 2 equiv. of *n*-butyllithium in tetrahydrofuran and then with 2 equiv. of methyl iodide, the reaction mixture is found to contain both the expected product, 1,2-bis(trimethylsilyl)1,2-dimethylhydrazine (I), and the rearranged product, 1,1-bis(trimethylsilyl)-2,2-dimethylhydrazine (II).



Pure 1,2-bis(trimethylsilyl)hydrazine, b.p. 147°, $n^{25}D$ 1.4253, d^{24}_4 0.834, was prepared by the method of Wannagat and Liehr.[1a,b,2] This material was shown to be the 1,2-isomer by reaction with phenyl isocyanate followed by hydrolysis to give hydrazine-N,N′-dicarboxylanilide, m.p. 245–248°, lit. m.p. 245°.[1h] That it was free of 1,1-isomer was shown by the n.m.r. spectrum which has a single peak in the Si–C–H region at τ 9.92.

In a typical experiment 4.1 g. (0.024 mole) of 1,2-bis(trimethylsilyl)hydrazine,[2] prepared by the method of Wannagat and Liehr,[1a,b] was treated with 0.048 mole of *n*-butyllithium in hexane at 0°. After being stirred for about 30 min. to ensure complete reaction, the mixture was chilled to −70°, and 25 ml. of freshly distilled tetrahydrofuran was added, causing the previously white suspension to become light yellow. Methyl iodide (0.48 mole) was then slowly injected. The mixture was then allowed to warm up slowly with stirring, filtered in a drybox, and fractionally distilled yielding 2.8 g. (60%) of pure colorless product, b.p. 67–71° (17 Torr). *Anal.* Calcd. for $C_8H_{24}Si_2N_2$: C, 46.99; H, 11.83; N, 13.70. Found: C, 47.33; H, 11.97: N, 13.62. The proton n.m.r. spectrum of the product shows two peaks at τ 9.98 and 9.89, assigned to trimethylsilyl protons, and two peaks at τ 7.43 and 7.37, assigned to the methyl protons in the two isomers. Relative peak areas are approximately 3:3:1:1, respectively, indicating that the two isomers must be present in nearly equal amounts. Partial separation of the mixture could be effected by fractional distillation.

The mixture was solvolyzed with 1-propanol to produce the mixed dimethylhydrazines which were treated with *p*-nitrobenzaldehyde yielding *p*-nitrobenzaldehyde dimethylhydrazone, m.p. 111–112, lit.[3] m.p. 111°, infrared spectrum identical with that of authentic *p*-nitrobenzaldehyde dimethylhydrazone. Isolation of this known hydrazone confirms the presence of the rearranged hydrazine in the original reaction mixture.

The rearrangement reported here, though not previously noted, may have occurred in previous reactions of silyl-substituted hydrazines with bases. Thus, in the reaction of 1-phenyl-2-trimethylsilylhydrazine with phenyllithium followed by bromine, a large amount of N-trimethylsilylaniline was observed as a by-product,[4] perhaps arising *via* a 1,2-silicon shift of the type described above. Many reactions of lithium derivatives of silylhydrazines have been reported in which structures of products are assigned without considering the possibility of rearrangement[1e,g]; some of these structures may now have to be reconsidered in the light of our evidence. At present it is not known whether the rearrangement occurs during or after treatment with *n*-butyllithium, or even conceivably during the reaction with methyl iodide. Investigations of these possibilities are under way, and studies of the limits and of the reaction in general are planned for the near future.

(1) (a) U. Wannagat and W. Liehr, *Angew. Chem.*, **69**, 783 (1957); (b) U. Wannagat and W. Liehr, *Z. anorg. allgem. Chem.*, **297**, 133 (1958); (c) U. Wannagat and H. Niederprum, *Angew Chem.*, **70**, 745 (1958); (d) U. Wannagat and W. Liehr, *Z. anorg. allgem. Chem.*, **299**, 341 (1959); (e) U. Wannagat and H. Niederprum, *ibid.*, **310**, 32 (1961); (f) H. Niederprum and U. Wannagat, *ibid.*, **311**, 270 (1961); (g) U. Wannagat, C. Krueger, and H. Niederprum, *ibid.*, **321**, 198 (1963); (h) U. Wannagat and C. Krueger, *Monatsh. Chem.*, **94**, 63 (1963).

(2) The material originally supposed by Wannagat and Liehr[1a,b] to be 1,2-bis(trimethylsilyl)hydrazine may have been a mixture of the 1,2- and 1,1-isomers (private communication from Professor U. Wannagat). The proportions of the two isomers formed in the reaction of trimethylchlorosilane with hydrazine depends on the reaction conditions in a way not yet fully understood. When present, the 1,1-isomer can easily be detected by n.m.r. spectroscopy (Si–C–H resonance at τ 9.99).

(3) O. L. Brady and G. P. McHugh, *J. Chem. Soc.*, **121**, 1648 (1922).

(4) U. Wannagat and C. Krueger, *Z. anorg. allgem. Chem.*, **326**, 288 (1964).