

**The Diamagnetic Anisotropy of a Borazine Ring. A
Reply to Muszkat's Correction**

Sir:

Muszkat¹ has given comments on our paper² in regard to the evaluation of diamagnetic anisotropy of a borazine ring. We were well aware of the difficulty in estimating $\chi_{||}$ of borazine and approximated it with that of isoelectronic benzene. This is a debatable problem to which Muszkat called our attention. However, we preferred the experimental $\chi_{||}$ of benzene to $\chi_{||}$ values of pyridine and other heterocycles calculated for a Kekulé-type structure by Pascal's additivity, because these compounds are not isoelectronic with borazine in a narrow sense (whereas *sym*-triazine, for instance, has 27 electrons in the 2s,2p orbitals of carbon or nitrogen and 3 electrons in the 1s orbitals of hydrogen, both borazine and benzene have 24 electrons in the 2s,2p orbitals of carbon, nitrogen, or boron and 6 electrons in the 1s orbitals of hydrogen) and also because Pascal's constant for nitrogen involves considerable complications in relation to bond types. Strictly speaking, one should take into account the exact shape and dimensions of bond orbitals occupied by electrons. In view of the lack of available data, we have made the bold assumption and hoped that, in spite of its approximate nature, our results would contribute to encourage future developments.

We further tried to confirm the adequacy of our assumption by estimation through Pascal's additivity rule taking into account constitutive correction constants. Muszkat's criticism is mainly directed to this point. Although our arguments are not convincing because of misprints involved and the approximate nature of Pascal's additivity rule, conclusions derived by us are not thereby altered. The magnetic susceptibility of boron trichloride, -62.0 (instead of -67.0), was taken from Landolt-Börnstein's Tables³ rather than from the table compiled by Foëx.⁴ This unfortunate error on our side must have made recalculation by Muszkat very difficult.

(1) K. A. Muszkat, *J. Am. Chem. Soc.*, **86**, 1250 (1964).

(2) H. Watanabe, K. Ito, and M. Kubo, *ibid.*, **82**, 3294 (1960).

(3) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Dritter Ergänzungsband, Dritter Teil, 5th Ed., Springer-Verlag, Berlin, 1936, p. 2180.

(4) G. Foëx, "Constantes Sélectionnées. 7. Diamagnétisme et Paramagnétisme," Masson et Cie, Paris, 1957.

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**Purine Deoxynucleosides. Synthesis of
9-(2'-Deoxy- α - and - β -D-ribofuranosyl and
2'-deoxy- α - and - β -D-ribofuranosyl)purines by the
Fusion Method¹**

Sir:

A simple and superior procedure has been developed for the synthesis of purine 2'-deoxyribofuranosides and purine 2'-deoxyribofuranosides which is of considerable utility and overcomes many of the limitations found in earlier work.

Most previously recorded syntheses of purine 2'-deoxynucleosides *via* a purine and an appropriate carbo-

hydrate derivative utilize a halosugar and a heavy metal (such as mercury or silver) salt to accomplish actual nucleoside formation.² This method is often characterized by inherent experimental difficulties and limitations including the arduous task of obtaining crystalline products due to purification problems. In view of these difficulties, numerous efforts have been made to devise new synthetic procedures for the preparation of purine 2'-deoxynucleosides. Schramm and co-workers³ employed 2-deoxyribose in the presence of polyphosphoric acid for the direct synthesis of 2'-deoxyadenosine. This method, however, is of questionable preparative value since Carbon⁴ has shown that under these conditions only a small yield of a mixture of at least six different deoxynucleosides was obtained.

A number of Japanese investigators⁵⁻⁸ have reported the acid-catalyzed fusion of 1,2,3,5-tetra-*O*-acetyl-D-ribofuranose and related D-ribofuranose derivatives with various purines to provide the corresponding β -D-ribofuranosylpurines in variable yield. Although omitted from several recent reviews covering the synthesis of purine nucleosides,² this adaptation of the Helferich glycosidation procedure⁹ now has been studied in our own laboratory and found to be of wide general application.^{9a} This type of reaction has now been utilized for a most convenient preparation of 9-(2'-deoxy- α - and - β -D-ribofuranosyl)purines. When 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose¹⁰ was fused with various purines, a good yield of an anomeric mixture of the corresponding 9-(2'-deoxy-D-ribofuranosyl)purine was obtained. This method has the advantage of simplicity, and in most instances the deoxynucleosides were crystallized directly from the reaction mixture after deacetylation.

Four grams of 6-chloropurine¹¹ and 10 g. of 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose¹⁰ were heated together to 127° in a preheated oil bath. Then a catalytic amount (75 mg.) of chloroacetic acid was added, and the temperature was maintained at 127° (oil bath temperature) for approximately 3 min. The acetic acid then was rapidly removed *in vacuo* and the melt was allowed to cool. The crude melt was dissolved in 30 ml. of hot methanol, and the solution was filtered to remove unreacted 6-chloropurine. The filtrate was treated with methanolic ammonia at 0° for 12 hr. After evaporation, the resulting residue was dissolved in hot ethyl acetate which on cooling yielded 2.6 g. of a crude anomeric mixture of crystalline nucleosides, m.p. 135-142°. Fractional crystallization from ethyl acetate containing a small volume of methanol gave 1.5 g. of fine needles¹² of 6-chloro-9-(2'-deoxy- α -D-ribo-

(2) For a review of syntheses of purine nucleosides, see J. A. Montgomery and H. J. Thomas, *Advan. Carbohydrate Chem.*, **17**, 301 (1962); A. M. Michelson, "The Chemistry of Nucleosides and Nucleotides," Academic Press, Inc., New York, N. Y., 1963, Chapter 2; T. L. V. Ulbricht, *Angew. Chem. Intern. Ed. Engl.*, **1**, 476 (1962).

(3) G. Schramm, H. Grotzsch, and W. Pollmann, *ibid.*, **1**, 1 (1962).

(4) J. A. Carbon, *Chem. Ind. (London)*, 529 (1963).

(5) T. Sato, T. Simadate, and Y. Ishido, *Nippon Kagaku Zasshi*, **81**, 1440 (1960); *ibid.*, **81**, 1442 (1960).

(6) T. Simadate, *ibid.*, **82**, 1268 (1961).

(7) T. Simadate, Y. Ishido, and T. Sato, *ibid.*, **82**, 938 (1961).

(8) Y. Ishido and T. Sato, *Bull. Chem. Soc. Japan*, **34**, 347, 1374 (1961).

(9) B. Helferich and E. S. Hillebrecht, *Chem. Ber.*, **66**, 378 (1933).

(9a) NOTE ADDED IN PROOF.—For recent application of the fusion method to nucleoside syntheses, see W. W. Lee, A. P. Martinez, G. L. Tong, and L. Goodman, *Chem. Ind. (London)*, 2007 (1963).

(10) H. Venner and H. Zinner, *Chem. Ber.*, **93**, 137 (1960). A new and improved synthesis of this compound will be reported later.

(11) A. Bendich, P. J. Russell, Jr., and J. J. Fox, *J. Am. Chem. Soc.*, **76**, 6073 (1954); see also A. G. Beaman and R. K. Robins, *J. Appl. Chem. (London)*, **12**, 432 (1962).

(12) Correct analyses for carbon, hydrogen, and nitrogen have been obtained for all 2-deoxy- α - and - β -D-ribofuranosyl- and ribopyranosylpurines prepared.

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