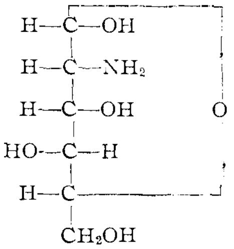
the molecular rotation of Compound 1 (+88)[8] approximates that of 1,6-anhydro-β-D-gulopyranose (+82) but contrasts with that of 1,6-anhydro-β-D-idopyranose (−103), we regard Compound 2 as 2-amino-2-deoxy-α-D-gulose (α-D-gulosamine) (I). This case apparently constitutes the first example


I

of a naturally occurring sugar with the gulose configuration.

The weakly reducing Compound C,[1] (crystalline hydrochloride, m.p. 215–220° dec.) (found: C, 34.57; H, 6.17; N, 16.20; Cl, 16.70) obtained from both streptothricin and streptolin B, is regarded as an intermediate hydrolysis product, since it yields, on prolonged treatment with aqueous acid, streptolidine and Compounds 1 and 2. Structural investigations of Compound C are in progress.

[8] Neither the α- nor β-forms of gulose or idose are reported in the literature.

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RECEIVED JULY 30, 1956

AN UNUSUAL FLUORINE MAGNETIC RESONANCE MULTIPLET[1]

Sir:

The nuclear magnetic resonance multiplets[2] which arise from the indirect coupling of nuclear spins[2,3] *via* their interactions with the electrons[2,4] in a molecule are of interest in relation to molecular and electronic structures. In those cases reported thus far, the magnitude of the coupling constant, A_{ij}, decreases monotonically with the number of chemical bonds separating nuclei i and j. However, we have found a molecule, $(CF_3)_2NCF_2CF_3$, in which the fluorine nuclei separated by four and five chemical bonds have considerably larger coupling constants (16 and 6 c.p.s.) than those separated by only three bonds (<1 c.p.s.).

The fluorine spectrum of the liquid has three main lines with chemical shifts, $10^5\ (H_r - H_c)/H_r$ referred to trifluoroacetic acid, of −1.99,[2] −0.84[3] and +2.31.[6] From the relative intensities, given in parentheses, the three lines are assigned to the $N{-}CF_2{-}$, $C{-}CF_3$ and $(CF_3)_2N$ groups. The spectra were obtained with a modified version[5] of our high resolution spectrometer.[6] The samples were provided by Dr. R. D. Dresdner of the University of Florida.

Under higher resolution, the three lines exhibit the multiplet structures reproduced in Figs. 1A, B and C, respectively. Figures 1A and B are septets, with relative intensities of 1:6:15:20:15:6:1, characteristic of coupling with six equivalent nuclei of spin 1/2. From this we conclude that the $(CF_3)_2N$ fluorine nuclei are coupled to both the $N{-}CF_2{-}$ and the $C{-}CF_3$ fluorine nuclei; the coupling constants are 16 and 6 c.p.s., respectively. On the other hand, there are no resonance components attributable to coupling between the fluorines in the $N{-}CF_2{-}$ and $C{-}CF_3$ groups. Any coupling between them is less than the line widths, which give an upper limit of about 1 c.p.s.

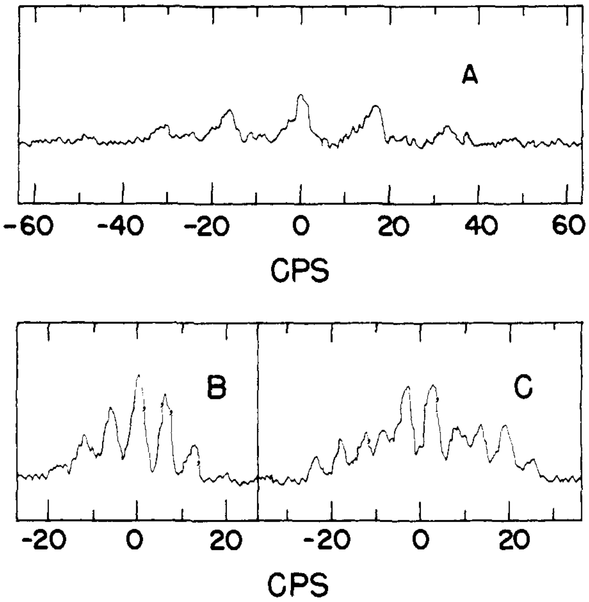

Fig. 1.—The high resolution fluorine magnetic resonance absorption spectrum of $(CF_3)_2NCF_2CF_3$, observed at a fixed frequency of 16.685 Mc. A, B and C are the absorption of the $N{-}CF_2{-}$, $C{-}CF_3$ and $(CF_3)_2N$ groups, centered at δ values of −1.99, −0.85 and +2.31, respectively.

These results show that there are two or more contributions to the F–F coupling, of comparable magnitude, with opposing signs, and attenuating at considerably different rates with the number of bonds between the fluorines. This interpretation is supported by the molecular orbital estimates made by McConnell[7] of the various interactions coupling the fluorine spins in fluoroethylenes.

A related though not as striking a case is that of the fluorobenzenes for which the dependence of the F–F coupling constant on orientation is $A_o >$

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[1] Assisted by the U. S. Office of Naval Research and by Grants-in-Aid from the E. I. du Pont de Nemours and Co. and from the Upjohn Co.

[2] H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

[3] E. L. Hahn and D. E. Maxwell, *Phys. Rev.*, **88**, 1070 (1952).

[4] N. F. Ramsey, *ibid.*, **91**, 303 (1953).

[5] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, in press (1956).

[6] H. S. Gutowsky, L. M. Meyer and R. E. McClure, *Rev. Sci. Instr.*, **24**, 644 (1953).

[7] H. M. McConnell, *J. Chem. Phys.*, **24**, 460 (1956).

$A_p > A_m$ (20, 13 and 7 c.p.s.) while the H–F coupling constants are $A_o > A_m > A_p$ (8.5, 6.5 and 2.2 c.p.s.).[8] Further experimental and theoretical studies of the H–H, H–F, and F–F coupling constants are in progress.

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[8] C. H. Holm, "Structural Applications of Radiofrequency Spectroscopy," Ph.D. Thesis, University of Illinois, 1955; to be published.

BOOK REVIEWS

Principles and Problems in Energetics. By J. N. BRØNSTED. Translated from the Danish by R. P. Bell, Balliol College, Oxford University. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y., 1955. vii + 119 pp. 15.5 × 23.5 cm. Price, $3.50.

In this book the author criticizes the classical presentation and some of the concepts of classical thermodynamics, gives a number of quotations from a great variety of authors to show that the concepts of heat, work and entropy are unsatisfactorily developed and presents an alternate development with special prominence to a generalization of the concept of work. In this generalization, the classical work done and the capacity of the system to do work are combined, so that, in a reversible process, Brønsted's "loss of work," $\Sigma\delta A_i = 0$.

Brønsted develops the concept of entropy rather differently from what he calls the classical development, stressing in particular the entropy production in an irreversible process. In addition to his generalization of the concept of work, he now writes $T\delta S'' = \delta Q''$ (p. 56) in which $\delta S''$ is the entropy production in the irreversible process, and $\delta Q''$ is a new quantity which Brønsted defines as the "energetic heat evolution." With these radical redefinitions of work and heat, Brønsted obtains the at first sight startling conclusion that the conversion of heat into work, as in the heat engine, is impossible. Work is undeniably obtained, but since he has lumped classical work and the capacity to do work in his "work," and a system of two reservoirs at T_1 and T_2, respectively, can be made to do work, this system obviously possesses the capacity to do work, and the work actually done plus the remaining capacity to do work is unchanged in a reversible process.

The general development of his concepts, along with criticisms of the "classical" viewpoints, and those of Carathéodory and Born, as shown by carefully selected quotations, occupy the first two-thirds of the book; the last third is devoted to applying these concepts to a number of specific cases, of which the greater part, the consideration of the bimetallic thermoelement and of the electrochemical cell with the electrodes at different temperatures, involves the assumption that the irreversible heat flow does not produce thermodynamically unpredictable disturbances.

Because of the reputation of the author, I commenced reading this monograph with anticipation of great pleasure and satisfaction, but ended it with a feeling of disappointment. To justify the presentation of a viewpoint different from that of classical thermodynamics, Brønsted quotes from a great variety of authors, including Mach and Planck, indicating that the concepts of heat and work are vague and unsatisfactory. Some of the sources quoted seem too unimportant to make his points, and it seems surprising that he makes no reference to Lewis' viewpoints,[1] particularly since his development of entropy is somewhat similar to that of Lewis, and the vagueness that he complains of in the use of heat and work is absent from Lewis' developments, where a gain of energy by means of thermal conduction or radiation is called heat absorbed, and a loss of energy by *other methods* is called work done. It is only energy *changes* during a *process* which deserve such distinctions; the energy of a mole of a chosen gas at 25° and 1 atmosphere is the same whether it attained this state by contact with a thermostat at 25°, by reversible compression from a lower temperature and pressure, or by any other process, reversible or irreversible, and it does not appear profitable to apportion this energy into "heat" and "work." In Brønsted's scheme, the interdiffusion of one mole of helium and one of neon (both here assumed perfect) at constant temperature would involve a "loss of work" equal to $2\,RT\ln 2$, and a like "energetic heat evolution," although no work in the ordinary sense has been done, and no energy, thermal or otherwise, has been exchanged with the surroundings, nor has the kinetic energy distribution amongst the molecules been altered.

Admitting that one can operate without logical contradictions with Brønsted's quantities (although with what seems unnecessarily roundabout bookkeeping of energy quantities), I strongly object to his appropriating the words *work* and *heat* for them. Too frequently scientists have "generalized" some older term until it became useless. A prime example is *air* in which case we were finally rescued by the invention of the word *gas*. If a new concept is developed, it should be given a new and distinctive name.

In spite of my disagreement with Brønsted's general thesis, I recommend the book to all serious students of thermodynamics and especially to teachers of the subject, for even if they reject his point of view they will be stimulated to re-examine and logically justify their own.

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Advances in Carbohydrate Chemistry. Volume 10. By MELVILLE L. WOLFROM, Editor, and R. STUART TIPSON, Assistant Editor. Academic Press, Inc., Publishers, 125 East 23rd Street, New York 10, N. Y. 1955. xx + 437 pp. 15.5 × 23 cm. Price $10.50.

With the advent of Volume 10, the utility of this well-established series to the practicing carbohydrate chemist is significantly enhanced. The present volume continues the exemplary tradition of its predecessors in providing an array of well-written, thorough and timely surveys on topics of interest to carbohydrate chemists in particular and to organic chemists in general.

The present eight chapters cover a broad range of interests. In "The Stereochemistry of Cyclic Derivatives of Carbohydrates" J. A. Mills summarizes and applies concepts of conformational analysis to the stability and chemistry of a number of carbohydrate derivatives. W. W. Binkley's survey of "Column Chromatography of Sugars and Their Derivatives" provides for the practitioner a useful complement to the treatment of paper chromatography which appeared in the previous volume. The preparation, properties, reactions and uses of several important classes of carbohydrate derivatives are delineated in chapters on "Glycosylamines" (G. P. Ellis and J. Honeyman) and "The Glycosyl Halides and Their Derivatives" (L. J. Haynes). The scope, mechanism and details of "The Amadori Rearrangement" are summarized by J. E. Hodge, and extensive Tables on "The Methyl Ethers of the Aldopentoses

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[1] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.