When heated above their melting points or with pyridine at 65°, both IIa and IIb were converted to the corresponding imides, as previously reported.[4]

N-Tolyl Phthalimides (IIIa and IIIb). Acid-Catalyzed Hydrolysis of Ia and Ib.—Hydrolysis of either Ia or Ib (3.44 g., 0.01 mole) with 5 *N* hydrochloric acid (10 ml., 0.05 mole) at reflux for 3 hr. resulted in high yields (2.0 g., 84%, from Ia; 1.9 g., 80%, from Ib) of the corresponding phthalimides, IIIa and IIIb. IIIa had a melting point of 182.5–183.0° (lit.[3] 182°), undepressed by admixture with an authentic sample prepared by a usual method[3a]; IIIb melted at 201–202° (lit.[4] 201–202°).

As previously reported,[4] IIIa and IIIb were converted to IIa and IIb, respectively, when heated on a steam cone for 1 hr. with 10% sodium hydroxide.

Acid-Catalyzed Hydrolysis of IIa and IIb.—Hydrolysis of IIa or IIb (2.55 g., 0.01 mole) with excess 5 *N* hydrochloric acid on a steam bath for 15 min. resulted in formation of *o*-phthalic acid (1.4 g., 84% in both cases). The product was identified by its infrared spectrum which was identical with that of an authentic sample.

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F^{19} Nuclear Magnetic Resonance Spectra of Some Benzotrifluorides

CARL L. BUMGARDNER

Gorgas Laboratory, Rohm and Haas Company,
Redstone Arsenal Research Division, Huntsville, Alabama

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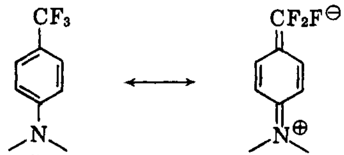
The electronic effect of the trifluoromethyl group attached to an aromatic ring and the dipole moment of *p*-dimethylaminobenzotrifluoride have been discussed in terms of resonance forms Ia,b.[1] If forms such as



Ia Ib

Ib are important, this effect might be reflected in the F^{19} n.m.r. spectrum. Taft, *et al.*,[2] have interpreted the F^{19} chemical shifts in various substituted fluorobenzenes as evidence for contributing forms IIa,b.

IIa IIb

To see if n.m.r. spectroscopy could be used to detect interactions exemplified by form Ib (negative hyperconjugation), we examined the benzotrifluorides collected in Table I.

Table I shows clearly that n.m.r. spectroscopy does distinguish between the *p*-aminobenzotrifluorides and all other compounds listed. In the same solvent there is little change in the spectra until the *p*-aminobenzotrifluorides are encountered. In methanol, for example, the ϕ^* values of *p*-nitrobenzotrifluoride and *m*-dimethylaminobenzotrifluoride differ by only 0.6 unit, whereas those of *m*-dimethylaminobenzotrifluoride and *p*-aminobenzotrifluoride differ by 1.4 units. The difference between *m*-dimethylaminobenzotrifluoride and *p*-dimethylaminobenzotrifluoride is even greater (1.8 units). A similar trend is shown by the values obtained in cyclohexane.

TABLE I

F^{19} N.M.R. SPECTRA OF BENZOTRIFLUORIDES

	Cyclohexane[a] ϕ^{*b}	Methanol[a] ϕ^{*b}
Benzotrifluoride	64.1	62.7
m-Nitrobenzotrifluoride	64.2	63.1
p-Nitrobenzotrifluoride	64.5	63.2
m-Aminobenzotrifluoride	63.9	62.9
m-Dimethylaminobenzotrifluoride	63.7	62.6
p-Aminobenzotrifluoride	62.2	61.2
p-Dimethylaminobenzotrifluoride	62.0	60.8

[a] Approximately 5% solutions by volume. [b] B. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

Resonance exemplified by Ia,b, which has been invoked to account for the high dipole moment of *p*-dimethylaminobenzotrifluoride,[1] also may be responsible for the unusual F^{19} n.m.r. spectra displayed by *p*-amino and *p*-dimethylaminobenzotrifluoride. Interestingly, Gutowsky, *et al.*,[3] who have compared the F^{19} n.m.r. spectra of several substituted benzotrifluorides and fluorobenzenes, observed that substituents affect the aromatic fluorine and trifluoromethyl fluorine resonances in an opposite manner.

Experimental

The *para* substituted benzotrifluorides in Table I and *m*-dimethylaminobenzotrifluoride were prepared according to directions given in ref. 1. The remaining compounds were purchased from Columbia Organic Chemicals Company, Columbia, South Carolina, or from Aldrich Chemical Company, Milwaukee, Wisconsin. N.m.r. spectra were obtained with a Varian Associates, Model V-3000-B, high resolution spectrometer using a 40-Mc. probe at 28°. Samples were measured with trichlorofluoromethane as internal standard by counting sideband frequencies. The CF_3 peaks were sharp and symmetrical in all cases.

Acknowledgment.—This research was carried out under Army Ordnance Contract Da-01-021 ORD-11878. We are grateful to Mr. Kirt Keller for technical assistance and to Mrs. Carolyn Haney for n.m.r. spectra.

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[1] J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950).

[2] R. W. Taft, Jr., R. E. Glick, I. C. Lewis, I. Fox, and S. Ehrenson, *ibid.*, **82**, 756 (1960).

[3] H. S. Gutowsky, D. W. McCall, B. R. McGarvey, and L. H. Meyer, *ibid.*, **74**, 4809 (1952).

Proton Nuclear Magnetic Resonance Analysis of Some Acylmetallocenes

M. D. RAUSCH AND V. MARK

Monsanto Chemical Company, Research and Engineering Division,
St. Louis, Missouri

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A gradual deshielding of the cyclopentadienyl ring protons in the metallocene series proceeding from ferrocene to ruthenocene to osmocene has been noted by

TABLE I

H¹ N.M.R. SPECTRA OF SOME ACYLMETALLOCENES

	Metallocene	Chemical shifts at ring positions, τ,[a] and multiplicity[b] C₅H₅ ring	 α	 β	Line separation in the apparent triplets, J, c.p.s.[a]
I	Ferrocene	5.86 (s)	. . .	. . .	. . .
II	Ruthenocene	5.45 (s)	. . .	. . .	. . .
III	Osmocene	5.30 (s)	. . .	. . .	. . .
IV	Acetylferrocene	5.82 (s)	5.23 (t)	5.51 (t)	1.9*0*
V	Acetylruthenocene	5.42 (s)	4.91 (t)	5.23 (t)	1.8*0*
VI	Acetylosmocene	5.21 (s)	4.77 (t)	5.06 (t)	1.6*5*
VII	1,1′-Diacetylferrocene	. . .	5.23 (t)	5.49 (t)	1.9*1*
VIII	1,1′-Diacetylruthenocene	. . .	4.88 (t)	5.19 (t)	1.8*2*
IX	1,1′-Diacetylosmocene[c]	. . .	4.73 (t)	5.03 (t)	1.6*7*
X	Benzoylferrocene	5.81 (s)	5.10 (t)	5.43 (t)	1.9*1*
XI	Benzoylruthenocene	5.39 (s)	4.82 (t)	5.16 (t)	1.8*0*
XII	Benzoylosmocene	5.18 (s)	4.68 (t)	4.99 (t)	1.6*5*
XIII	1,1′-Dibenzoylferrocene	. . .	5.08 (t)	5.43 (t)	1.9*3*
XIV	1,1′-Dibenzoylruthenocene	. . .	4.76 (t)	5.12 (t)	1.8*2*
XV	1,2-Dibenzoylruthenocene	5.23 (s)	4.83 (d)	5.07 (t)	2.5*0*

[a] Values given were measured on an expanded (50 c.p.s.) scale and are estimated to be accurate to within ±0.02 unit. [b] s = singlet d = doublet, t = apparent triplet (except for XV, in which a true triplet is observed). [c] The ratio of intensities of the α, β, and acety protons (7.91 τ) is 4:4:6. The presence of very weak singlets at 5.12 and 7.68 τ is probably due to a minor amount of a homoannular diacetylosmocene.

several investigators.[1-3] We have undertaken the n.m.r. analysis of several mono- and diacylmetallocenes in order to examine the generality of these observations, to compare quantitatively the $\Delta\tau$-values for each set of acylmetallocenes, and to obtain information regarding the coupling interactions of acylmetallocene ring protons as a function of the metal.

The nuclear magnetic resonance spectra of the acylmetallocenes are summarized in Table I, together with the n.m.r. constants of the parent metallocenes. Analysis of the data by comparison of related structures and, within the groups, of pertinent portions of the molecules, indicates a linear relationship of remarkable consistency.

The presence of both the acetyl and the benzoyl group in the metallocene molecule is reflected by a deshielding of not only the hydrogens alpha and beta to the acyl group, but also by a consistent, although smaller, deshielding of the nonsubstituted ring. As indicated by Pople[4] and by Jackman,[5] the diamagnetic anisotropy of the carbonyl group effects positive shielding in conical regions above and below the plane of the double bond and negative shielding (deshielding) elsewhere. A coplanarity of the carbonyl group with the cyclopentadienyl ring thus leads to a deshielding of the protons of the same ring, and, depending on the shape and dimensions of the positive shielding cone of the carbonyl group, to a deshielding or shielding of the unsubstituted ring hydrogens. If there were no rotation of the rings around the center axis, more than one signal would result from the protons of the unsubstituted ring. The presence of only one signal in the second ring of IV–VI and X–XII is consistent with earlier evidence for an essentially free rotation of the rings in ferrocene.[6] The observed singlet in the n.m.r. spectra of monoacylmetallocenes thus represents an averaged frequency of the unsubstituted ring protons. The small, but consistent, low field shifts[7] can be due to several factors. The unsubstituted ring could lie in the negative zone of the carbonyl cone so that the deshielding effect is dominating. Inductive deactivation across the metal atom might also contribute to the observed trend.[8]

In comparison with the monoacetylmetallocenes, the monobenzoyl derivatives X–XII showed a more enhanced effect on the relative chemical shifts. Such an enhancement in the deshielding of the protons alpha and beta to the acyl group was anticipated due to the presence of the additional deshielding effect of the phenyl ring. The strong negative shift is indicative of the coplanarity of the cyclopentadienyl and phenyl rings with the carbonyl group.

Parallel with the effect on the unsubstituted ring is the strong deshielding by the acyl groups on the α- and β-hydrogens of the substituted cyclopentadienyl ring. Both the α- and β-protons have the appearance of well resolved triplets.[9] The more deshielded protons were assigned as being alpha to the acyl group on the basis of the effect of the acetyl group on ring protons in the benzene series[10] and on the basis of the analysis of 1,2-dibenzoylruthenocene (*vide infra*). The deshielding effect of the carbonyl group is thus felt to a lesser extent in the more distant β-position than in the adjacent α-position. Such a difference between the effect on the α- and β-protons parallels analogous cases in benzene substituted by carbonyl and nitro groups. The

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(1) T. J. Curphey, J. O. Santer, M. Rosenblum, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5249 (1960).

(2) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *ibid.*, **82**, 5846 (1960).

(3) D. E. Bublitz, W. E. McEwen, and J. Kleinberg, *ibid.*, **84**, 1845 (1962).

(4) J. A. Pople, *Proc. Roy. Soc.* (London), **A239**, 541, 550 (1957).

(5) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, pp. 121–125.

(6) M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958).

(7) The observation that the protons of the unsubstituted cyclopentadienyl ring in monoacetylferrocene appear at a higher field than those of ferrocene when the spectrum is determined in benzene solution [K. L. Rinehart, Jr., D. E. Bublitz, and D. H. Gustafson, *ibid.*, **85**, 970 (1963)] is in accord with recent findings of R. E. Klinck and J. B. Stothers [*Can. J. Chem.*, **40**, 2329 (1962)]. The phenomenon of increased shielding in benzene solution is interpreted by the latter authors as being caused by a specific solute-solvent interaction of preferred geometry.

(8) For a review and discussion of interannular electronic effects in ferrocene, see M. D. Rausch, *ibid.*, in press.

(9) Although these triplets are themselves not symmetrical, there is a plane of symmetry between them, in accordance with an A_2B_2 system.

(10) See ref. 5, p. 63.

difference in the frequency between the α- and β-protons in the acetylmetallocene series, 0.28–0.32 p.p.m., is in the same order as the frequency difference between the *ortho* and *meta* protons in acetophenone (0.36 p.p.m.). Similarly, in the benzoylmetallocene series, the difference between the α- and β-frequencies is 0.31–0.34 p.p.m.

The extent of deshielding of the α- and β-protons in acetylmetallocenes, with respect to the parent metallocene, is also found to match closely the deshielding encountered in the benzene series. A comparison of the $\Delta\tau$ values with the extent of deshielding of the *ortho* and *meta* hydrogens in acetophenone (with respect to the proton resonance of benzene)[10] indicates a close coincidence. The $\Delta\tau$ values of -0.63 and -0.27 p.p.m. for the *ortho* and *meta* hydrogens in acetophenone are thus matched with corresponding -0.63 and -0.35 p.p.m. values for the α- and β-protons, respectively, in acetylferrocene. A similar set of values is also obtained from the frequencies of acetylruthenocene (-0.54 and -0.22 p.p.m.) and acetylosmocene (-0.53 and -0.24 p.p.m.). The $\Delta\tau$-values for the α- and β-protons in 1,1′-diacetylmetallocenes exhibit a similar relationship, the constants being -0.63 and -0.37 p.p.m. in the ferrocene, -0.57 and -0.26 p.p.m. in the ruthenocene, and -0.57 and -0.27 p.p.m. in the osmocene derivatives.

In the benzoylmetallocene series, an added deshielding due to the phenyl group should be expected. Indeed, the replacement of a methyl by a phenyl group in the acylmetallocenes causes an additional deshielding of the α-protons by 0.13 and 0.09 p.p.m. in the ferrocene and ruthenocene series, and of the β-protons by 0.08 and 0.07 p.p.m. in this series. The corresponding figures in the 1,1′-dibenzoyl series are 0.15 and 0.12 p.p.m. for the α-protons and 0.06 and 0.07 p.p.m. for the β-protons. The deshielding effect of the replacement of the methyl by a phenyl group in these acylmetallocenes can be compared to the known deshielding of the cyclopentadienyl protons by a phenyl substituent attached directly to the ring. The β-protons in *p*-nitrophenylferrocene, for example, are deshielded by 0.4 τ with respect to ferrocene.[11]

The consistent behavior of the α, β, and unsubstituted ring protons with respect to the acetyl and benzoyl substituents is also matched by the regularity in the variation of the proton frequencies with respect to changing the metal. A presentation of this data in the form of a diagram is given in Fig. 1, where the proton frequencies (in τ) are given for metallocenes containing either iron, ruthenium or osmium central atoms. Every series examined shows a gradual deshielding of *all* the corresponding ring protons proceeding from the ferrocene to the ruthenocene and osmocene derivatives. All of the series also indicate a larger difference between the proton frequencies of the ferrocene and ruthenocene derivatives than between the latter and the osmocene analogs. The order of decreased shielding of the ring protons parallels qualitatively the order of decreasing reactivities in electrophilic substitution reactions of the ferrocene, ruthenocene, and osmocene triad,[12] and parallels further the order of increasing reactivity of the ring protons toward *n*-butyllithium.[12]

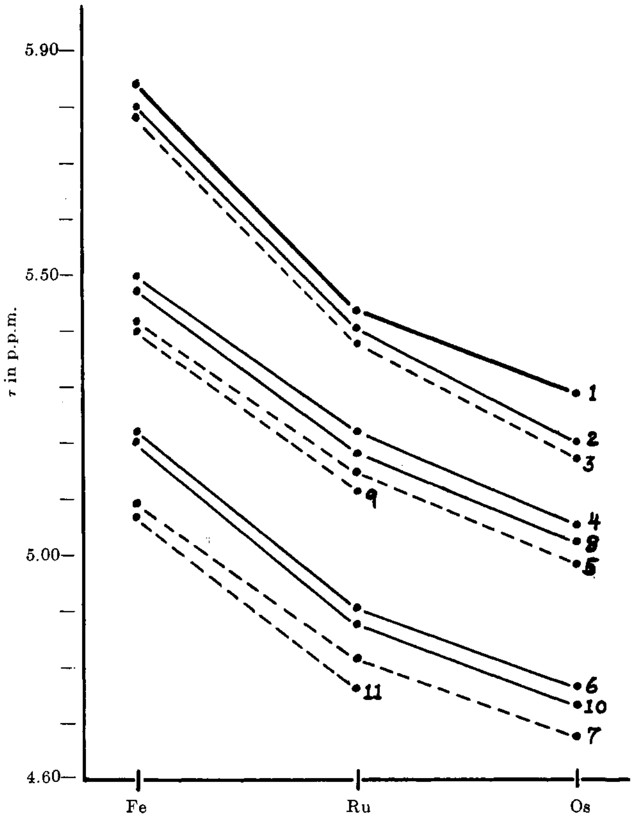

Fig. 1.—Variation of the proton frequencies in the n.m.r. spectra of acylmetallocenes: (1) H in metallocenes; (2) H′ in monoacetylmetallocenes; (3) H′ in monobenzoylmetallocenes; (4) H_β in monoacetylmetallocenes; (5) H_β in monobenzoylmetallocenes; (6) H_α in monoacetylmetallocenes; (7) H_α in monobenzoylmetallocenes; (8) H_β in 1,1′-diacetylmetallocenes; (9) H_β in 1,1′-dibenzoylmetallocenes; (10) H_α in 1,1′-diacetylmetallocenes; (11) H_α in 1,1′-dibenzoylmetallocenes.

A relationship in which a similar trend is reflected is obtained from a comparison of the line separation in the apparent triplets with the changing of the metal atom. The differences, although small, are nevertheless reproducible and probably indicate that the coupling between the ring protons in acylmetallocenes decreases from the iron to the ruthenium to the osmium derivatives. Contrary to the differences in the chemical shifts, however, the decrease in the line separation in the apparent triplets between the ruthenocenes (1.80 cp.s.) and osmocenes (1.65 c.p.s.) is somewhat greater than between the ferrocenes (1.90 c.p.s.) and ruthenocenes.[13]

The position and shape of the resonance lines permit the assignment of structures to isomers in substituted metallocenes. For example, the isolation of a dibenzoylruthenocene, m.p. 141.8–142.4°, from the benzoylation of ruthenocene was shown by infrared analysis to be a homoannular dibenzoylruthenocene, although the position of the benzoyl groups within the

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(11) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High-Resolution N.M.R. Spectra Catalog," Spectrum No. 321, Varian Associates, Palo Alto, Calif.

(12) M. D. Rausch, E. O. Fischer, and H. Grubert, *J. Am. Chem. Soc.*, **82**, 76 (1960).

(13) Coincidentally, a similar sequence is found in the in-plane bending modes of the ring hydrogens of the metallocene triad, where the ruthenocene frequency (1001 cm.$^{-1}$) is closer to the ferrocene mode (1002 cm.$^{-1}$) than to the osmocene mode (995 cm.$^{-1}$) [ref. 12; E. R. Lippincott and R. D. Nelson, *J. Chem. Phys.*, **21**, 1307 (1953); *J. Am. Chem. Soc.*, **55**, 4990 (1955); *Spectrochim. Acta*, **10**, 307 (1958)].

substituted ring was not determined.[3,14] The n.m.r. spectrum of this product indicates three kinds of cyclopentadienyl ring protons by the presence of three frequencies at 4.83, 5.07, and 5.23 τ with intensities of 2.0:1.0:5.0. The lines represent a doublet, a triplet, and a singlet, respectively, with $J = 2.5$ c.p.s. The frequency of the doublet matches closely the value for the α-protons in benzoylruthenocene (4.82 τ), and the frequency of the triplet is close to that of the β-protons in benzoyl- (5.16 τ) and 1,1′-dibenzoylruthenocene (5.12 τ). A 1,2-dibenzoyl structure is thus indicated for the isomer with m.p. 141.8–142.4°. For 1,3-dibenzoylruthenocene, a low field triplet and a higher field doublet near 4.76–4.83 τ with an intensity ratio of 1:2 may be anticipated, in addition to a frequency for the unsubstituted ring hydrogens at about 5.2 τ.[15]

The identification of the homoannular dibenzoylruthenocene as the 1,2-isomer lends some support to the prediction, based on molecular orbital calculations,[16,17] that in electrophilic substitution reactions of ferrocene derivatives bearing electron-withdrawing groups, the 2-position is somewhat favored over the 3-position. By contrast, the descriptive resonance treatment indicates the 3-position as the preferential site of attack. The identification of homoannular diacetylferrocene as the 1,2-isomer[6,16] is thus paralleled by the isolation and identification of 1,2-dibenzoylruthenocene, and both support the molecular orbital prediction concerning site reactivities in monoacylmetallocene derivatives. The support for this interpretation is rendered even stronger when one considers the increased bulkiness of the benzoyl substituent.

The occurrence of well resolved and well separated lines in the n.m.r. spectra of various metallocene derivatives designate these compounds as suitable substrates for the study of substituent effects on the ring protons. The simplicity of the spectra allows the study of substituents and the assignment of modes in cases where the analogous operations in benzenoid systems are rendered difficult due to the multiplicity of lines resulting from long-range interactions.

Experimental

1,1′-Diacetylosmocene was isolated from the reaction of osmocene with a large molar excess of acetic anhydride and phosphoric acid. The general procedure of Hill and Richards was used,[18] except that the reaction was made on a fourfold larger scale. Chromatography of the reaction product from such a run, using benzene and benzene–ethyl ether mixtures on alumina, produced 0.050 g. of osmocene, m.p. 227–228°, 1.64 g. of acetylosmocene (91%), m.p. 130.5–131.5° (lit.[18] m.p. 129.5–130°), and 2.0 mg. of a yellow crystalline solid. The latter was recrystallized from *n*-heptane to produce 1.6 mg. (0.1%) of 1,1′-diacetylosmocene, m.p. 148–152°. The n.m.r. spectrum of this product in deuteriochloroform solution is consistent with the proposed formulation (see Table I).

Homoannular dibenzoylruthenocene was generously supplied by Prof. W. E. McEwen. All other metallocenes used in this study were analytically pure samples and were prepared by methods reported in the literature.[12,18]

N.m.r. spectra were determined on a Varian Model A-60 spectrometer as 10% (weight to volume) solutions in deuteriochloroform. In several comparative spectra in which the sample concentrations were varied from 5 to 10%, no effect due to dilution could be detected.

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[14] D. E. Bublitz, J. Kleinberg, and W. E. McEwen, *Chem. Ind.* (London), 936 (1960).

[15] A similar interpretation also applies for the n.m.r. frequencies of 1,3-diacetylferrocene. In accord with these predictions is the finding that the peak of area two is at a higher field than the peak of area one in the n.m.r. spectrum of 1,3-diacetylferrocene (K. L. Rinehart, Jr., and A. F. Ellis, personal communication).

[16] J. H. Richards and T. J. Curphey, *Chem. Ind.* (London), 1456 (1956).

[17] M. Rosenblum and W. G. Howells, *J. Am. Chem. Soc.*, **84**, 1167 (1962).

[18] R. A. Hill and J. H. Richards, *ibid.*, **83**, 3840 (1961).

The Synthesis of a Glucosamine–Asparagine Compound. Benzyl N^2-Carbobenzyloxy-*N*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-L-asparaginate[1]

COLIN H. BOLTON[2] AND ROGER W. JEANLOZ

Laboratory for Carbohydrate Research,
Departments of Biological Chemistry and Medicine,
Harvard Medical School and the Massachusetts General Hospital,
Boston, Massachusetts

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In the course of the study of the link between the carbohydrate and protein parts of egg albumin, a glycosylamine type of linkage has been proposed by Johansen, Marshall, and Neuberger[3] and by Nuenke and Cunningham.[4] The carbon at position 1 of 2-acetamido-2-deoxy-D-glucose (*N*-acetyl-D-glucosamine) would be linked to the amide group of asparagine. Such a structure also has been suggested by other investigators[5] for egg albumin and seems also to agree with the experimental data obtained in the study of γ-globulins.[6,7] It recently has been proposed for the linkage of the carbohydrate part to the protein part of the α_1-acid glycoprotein of human plasma.[8,9]

As a part of the study carried out on the structure of the carbohydrate component of the α_1-acid glycoprotein of human plasma,[10] the synthesis of a glucosamine–asparagine compound, possessing the above-proposed structure, namely benzyl N^2-carbobenzyloxy-*N*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-L-asparaginate (VIII), was undertaken.

A first approach was an attempt to condense L-aspartic acid with a benzylidene derivative of D-glucosamine: a β-D-glucosylamide compound of D-glucose and L-aspartic acid has been first obtained by

[1] Amino Sugars XXXVI. This is publication No. 340 of the Robert W. Lovett Memorial Group for the Study of Crippling Diseases, Harvard Medical School at the Massachusetts General Hospital. This investigation has been supported by research grants from the American Cancer Society (Institutional Grant 42-B) and from the National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, United States Public Health Service (Grant A-3564-C1). Preliminary reports describing this work have been presented at the International Colloquium on Glycoproteins and on the Biochemistry of Connective Tissue in Normal and Pathological States, Paris, June, 1962, and before the Division of Carbohydrate Chemistry at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

[2] Department of Organic Chemistry, The University, Bristol, England.

[3] P. G. Johansen, R. D. Marshall, and A. Neuberger, *Biochem. J.*, **78**, 518 (1961).

[4] R. H. Nuenke and L. W. Cunningham, *J. Biol. Chem.*, **236**, 2452 (1961).

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[7] C. Nolan and E. L. Smith, *J. Biol. Chem.*, **237**, 453 (1962).

[8] E. H. Eylar, *Biochem. Biophys. Res. Commun.*, **8**, 195 (1962).

[9] S. Kamiyama and K. Schmid, *Biochim. Biophys. Acta*, **63**, 266 (1962).

[10] E. H. Eylar and R. W. Jeanloz, *J. Biol. Chem.*, **237**, 622, 1021 (1962); R. W. Jeanloz and A. M. Closse, *Federation Proc.*, **22**, 538 (1963).