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N. M. R. STUDIES ON NITROGEN-CONTAINING SUGAR DERIVATIVES SUBSTITUTED BY ^{15}N. PART III. : THE NATURE OF THE CHELATIONS IN SUGAR OSAZONE-FORMAZANS.

by L. Mester and G. Vass

Institut de Chimie des Substances Naturelles du C. N. R. S., 91 - Gif s/Yvette,
Centre National de la Recherche Scientifique, Paris, France.

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The first osazone-formazan (formazyl-ketone phenylhydrazone) in the sugar series was prepared in 1955 through the action of diazotized aniline on D-glucosazone (D-*arabino*-hexulose phenylosazone) (1). ^{14}C-labelled compounds were used by Mester and Weygand (2) to prove the presence of a bis-chelated structure in D-glucosazone-formazan ([D-*arabino*-tetrahydroxy-butyl] -formazyl-ketone phenylhydrazone).

Substitution of ^{15}N in sugar osazones (3) and sugar formazans (4) permitted the study of the nature of the chelation by N. M. R. The same method is used now to prove the structure of sugar osazone-formazans and to obtain further information concerning the exact nature of the chelation in these sugar derivatives.

The N. M. R. spectrum (Fig. II. 1) of the tetra-O-acetyl D-glucosazone-formazan ([D-*arabino*-tetrahydroxy-butyl] -formazyl-ketone phenylhydrazone tetra-O-acetate) shows the presence of two chelated N-H signals : one at 11.8ppm corresponding to the N-H signal of the osazone portion, another at 15.5ppm corresponding to the N-H signal of the formazan fragment of the molecule ($CDCl_3$; TMS ; 60 MHz).

We first introduced ^{15}N in the α_1 position through the action of diazotized aniline-^{15}N (enrichment 99%) on D-glucosazone (Fig. I : Scheme A). The tetra-O-acetyl derivative of the labelled compound showed in deuteriochloroform (TMS, 60MHz) a doublet (J = 46cps) (Fig. II, 2), instead of the sharp chelated N-H singlet at 15.5ppm of the non-labelled compound. The same coupling constant was observed for the simple formazans when substituted by ^{15}N in the α_1 position. This observation suggests a rapid tautomerization in the formazan chelated ring of the sugar osazone-formazans. According to the reported I. R. spectral data (5) of the formazans, as well as theoretical considerations (6), the presence of a symmetrical mesomeric structure is less probable.

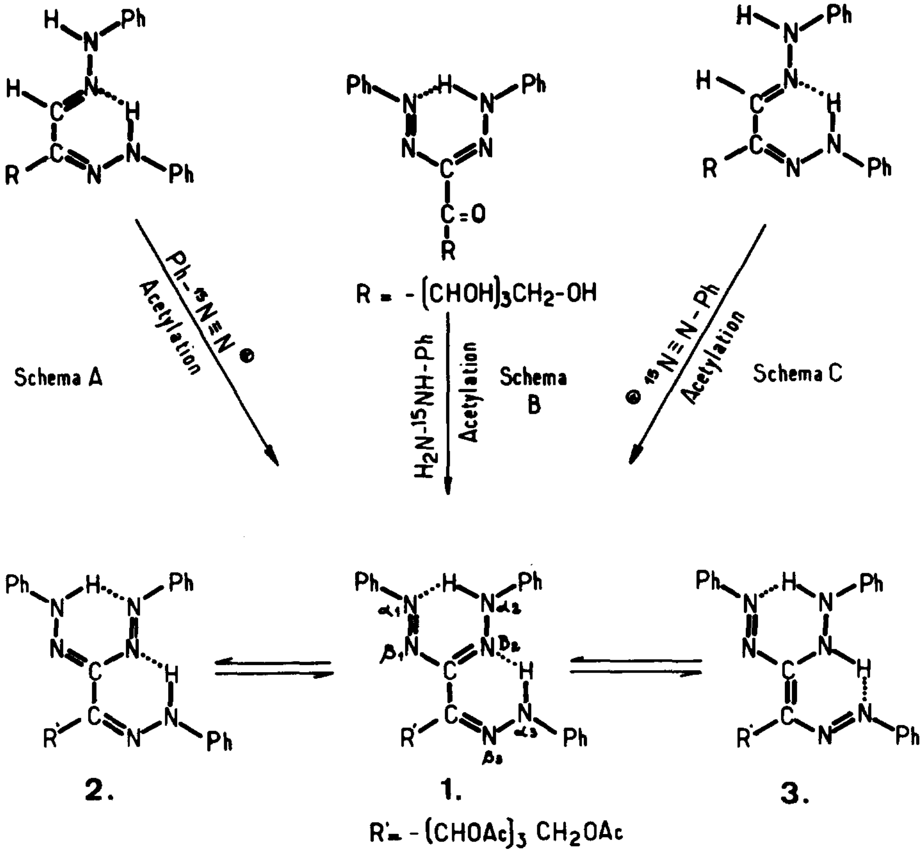
Schema A
Ph-^{15}N≡N ⊕
Acetylation
R = -(CHOH)$_3$CH$_2$-OH
H$_2$N-^{15}NH-Ph
Acetylation
Schema B
⊕ ^{15}N≡N-Ph
Acetylation
Schema C
2.
1.
3.
R' = -(CHOAc)$_3$ CH$_2$OAc

FIG.I

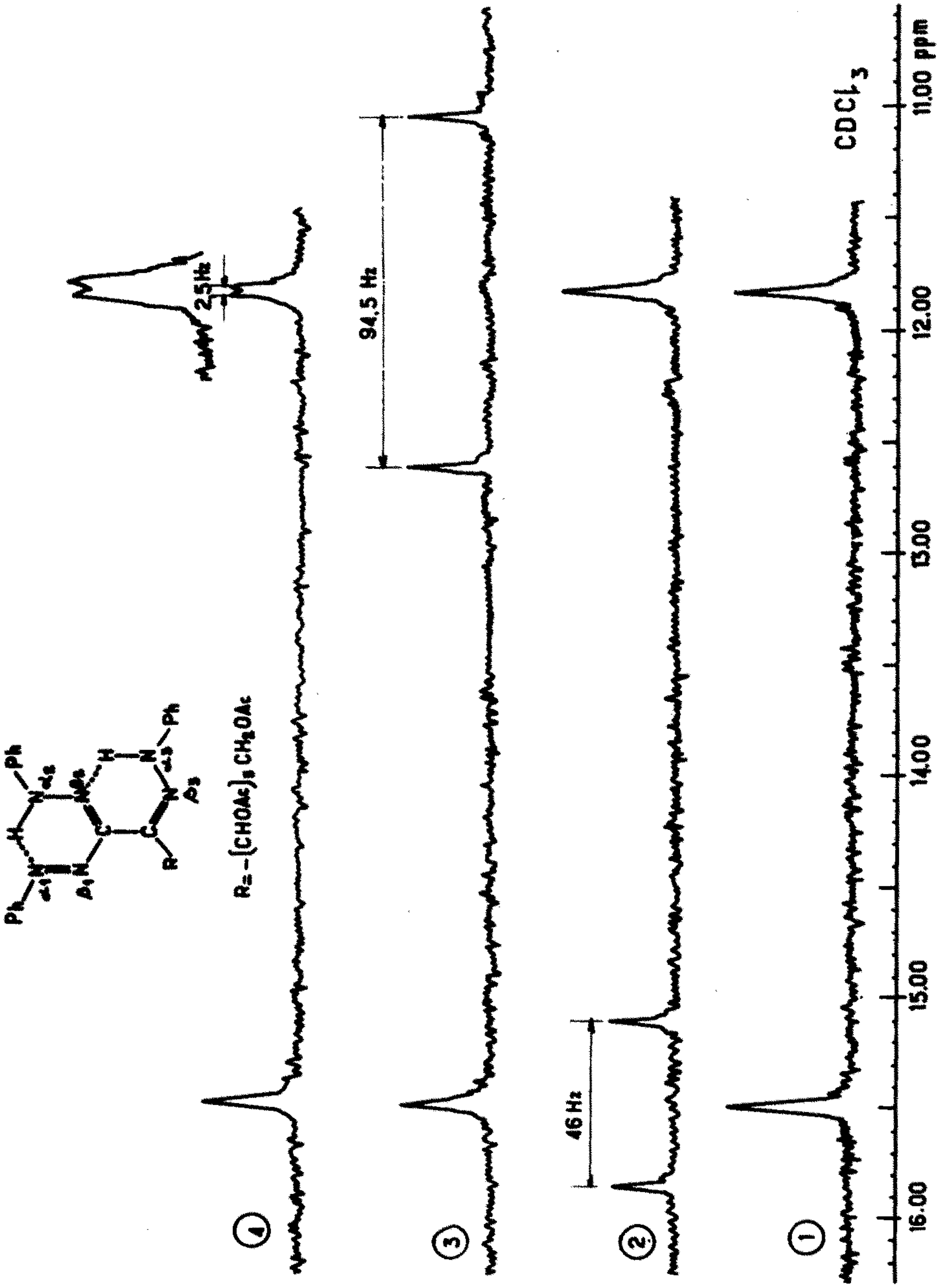
Ph
Ph
Ph
Ph
R
$R = -(CHOAc)_3CH_2OAc$
④
③
②
①
2,5 Hz
94,5 Hz
46 Hz
$CDCl_3$
16.00
15.00
14.00
13.00
12.00
11.00 ppm

FIG.II

We then substituted ^{15}N in the α_3 position through the action of phenylhydrazine-^{15}N (enrichment 99%) on D-glucosone-formazan ([D-arabino-tetrahydroxy-butyl]-formazyl-ketone) (7) (Fig. I : scheme B). The chelated N-H signal at 11.8ppm of the osazone portion of the molecule appeared as a doublet, J = 94.5cps ($CDCl_3$; TMS ; 60MHz) (Fig. II. 3). The same value was observed for sugar osazones when substituted by ^{15}N in the same position.

Finally, we substituted the molecule in the β_1 position through the action on D-glucosazone of aniline diazotized by $Na^{15}NO_2$ (enrichment 99%) (Fig. I : Scheme C).

Because of the free rotation around the C_1-C_2 bond the ^{15}N atom transfers rapidly between the β_1 and β_2 sites which it occupies with the same probability on time average (2). The chelated N-H proton in the α_3 position is coupled with this ^{15}N atom and therefore, its signal ($CDCl_3$; TMS ; 60MHz) is expected to be a doublet as observed with an averaged coupling constant (J = 2.5Hz) (Fig. II. 4). This observation suggests a direct interaction between the formazan-ring and the C-2 phenylhydrazone and confirms the bis-chelated structure of sugar-osazone-formazans.

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