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^{73}Ge NMR spectra of 1,3-dioxa-6-aza-2-germacyclooctanes

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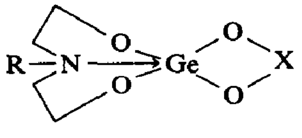
Abstract

The spirocyclic derivatives of 1,3-dioxa-6-aza-2-germacyclooctanes (II) have been studied by ^{73}Ge NMR spectroscopy. Evidence for the existence in II of a transannular donor–acceptor N → Ge bond is presented.

Until recently the only derivatives of pentacoordinate Ge studied by ^{73}Ge NMR were the germatranes $ROGe(OCH_2CH_2)_3N$ (I) containing an intramolecular donor–acceptor (DA) N → Ge bond [1,2]. Here we report ^{73}Ge NMR study of the bicyclic analogues of I, i.e. 1,3-dioxa-6-aza-2-germacyclooctanes (germocanes, II).



(II)

(1: $X = (CH_2)_2$;
2: $X = (CMe_2)_2$;
3: $X = o\text{-}C_6H_4$;
4: $X = (CH_2CH_2)_2O$)

a: $R = H$
b: $R = Me$
c: $R = Pr^i$

An increase in ^{73}Ge shielding in derivatives of II (see Table 1), as compared to that observed for the model compound $Ge(OEt)_4$ [3], provides evidence for the existence of a transannular DA N → Ge bond in II in solution. This agrees well with the results of an X-ray diffraction study of crystalline 1b in which the distance between the N and Ge atoms is decreased to 2.159 Å [4]. Substitution of the H atom at N by a Me or Pr^i group does not appreciably affect the ^{73}Ge shielding and, consequently the DA N → Ge bond strength.

The insignificant upfield shift of the ^{73}Ge resonance in **2b** compared with that of **1b** is attributable to the inductive effect of the Me groups in the β-position which is consistent with the effects observed in tetraalkoxygermanes [3]. A similar effect is observed for compound **3b**, but the lack of ^{73}Ge data for the appropriate model compounds prevents definite conclusions to be drawn.

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Table 1

^{73}Ge NMR data for 1,3-dioxa-6-aza-2-germacyclooctanes (II) in CD_3CN at 343 K and for model compounds [a]

Compound	δ ^{73}Ge	$\Delta\nu_{1/2}$
1a	-57	280
1b	-55	320
1c	-56	500
2b	-57	170
3b	-82	150
4a [b]	-94	240
$Ge(OEt)_4$ [c]	-44	30
$N(CH_2CH_2O)_3GeOEt$ [d]	-68	165

[a] Chemical shifts (δ) in ppm relative to Me_4Ge, linewidth at half-height ($\Delta\nu_{1/2}$) in Hz. ^{73}Ge NMR spectra were recorded on a Bruker WM-360 spectrometer at 12.56 MHz in 5-mm sample tubes. [b] In DMSO-d_6. [c] Ref. 3. [d] In $CDCl_3$, ref. 1.

Decreased ^{73}Ge shielding in the series **1** and **2**, as compared to the alkoxy derivatives of I (δ ^{73}Ge = -60 to -68 ppm [1,2]), suggests a stronger DA N→Ge bond in compounds I. However, the differences in the conditions under which ^{73}Ge spectra were recorded must be taken into account.

A substantial increase in ^{73}Ge shielding in compound **4a** is indicative of a pseudohexacoordinate Ge resulting from additional 1,5-transannular O→Ge bonding. At present, unambiguous interpretation of the results obtained is not possible because of insufficient information regarding the influence of ring size on the ^{73}Ge chemical shifts.

The strong temperature dependence of the ^{73}Ge linewidth is also indicative of the existence of DA N→Ge bonding in II. For most of the II derivatives the linewidth at half-height of the ^{73}Ge resonance was ca. 200 Hz (see Table 1) and was found to rise with fall in temperature. Only compound **4a** gave ^{73}Ge signals at ambient temperature in DMSO-d_6 solution. The enhanced asymmetry of the charge distribution around Ge in the pentacoordinate state results in an increase in quadrupolar relaxation rate of the ^{73}Ge nuclei, thus no ^{73}Ge signals were observed for the other compounds at ambient temperature in DMSO-d_6.

Consequently, the ^{73}Ge NMR data favour the existence of an intramolecular N→Ge coordination bond in 1,3-dioxa-6-aza-2-germacyclooctanes in solution.

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