Electron density distributions in substituted 2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-dienes studied by NMR spectroscopy

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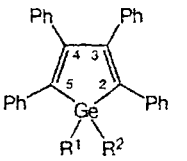
The signals in the ^{13}C NMR spectra of 2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-dienes ($R^1 = R^2 = H$, Me, *cyclo*-C_3H_5, $SiMe_3$, $SnMe_3$, $R^1 = Me$, $R^2 = H$, Cl) were completely assigned using 2D NMR spectroscopy. The pattern of the variation of the chemical shifts in the ^{13}C NMR spectra indicates that the effects of substituents R^1 and R^2 on the heterocycle and on the phenyl groups are of inductive rather than mesomeric origin and include the direct through-space polarization of bonds (field effect).

Key words: germanium, 1-germacyclopenta-2,4-dienes, germoles, ^{13}C NMR.

In recent years, heteroanalogs of cyclopentadiene, 1-sila(germa,stanna)cyclopenta-2,4-dienes (metaloles) have attracted increasing interest.[1,2] The stability of these heterocyclic compounds increases substantially when alkyl or aryl substituents are introduced into the ring.[1,2] Therefore, substituted metaloles are convenient objects for the investigation of the structures of heterocyclopentadienes by physicochemical methods. Stable 2,3,4,5-tetraphenylmetaloles, which are easily prepared by the reaction of the dilithium salt of tetraphenylbutadiene with the corresponding dichloride $R^1R^2ECl_2$ (E = Si, Ge, Sn), are the most accessible from the synthetic viewpoint.[1] Therefore, 2,3,4,5-tetraphenylmetaloles most often become the objects of studies including physicochemical studies.[1,2] The problem of the electron density distribution in the ring and the effect of the substituents at the heteroatom on it remains an important aspect of the studies of these derivatives.

Information on the distribution of electron density can be obtained using NMR spectroscopy. Since the effect of anisotropic factors on the shielding of carbon atoms is considerably less pronounced than their effect on the shielding of protons, it is ^{13}C NMR spectroscopy that is often used to study the electron density distribution in molecules.

Although a lot of data on the ^{13}C NMR spectra of germoles have been published,[1] only in recent years have attempts been made to carry out detailed analysis and correct assignment of the signals, in particular, in the spectrum of 2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-dienes (**1**).[2–6] However, the results obtained are often contradictory; this is not surprising, because it is necessary to assign the chemical shifts of the carbon atoms of the germacyclopentadiene ring (C(2,5) = α-C and C(3,4) = β-C) and those of the phenyl substituents in the α- and β-positions (α-C_{ipso}, β-C_{ipso}, α-C_o, β-C_o, α-C_m, β-C_m, α-C_p, and β-C_p). Only recently, using 2D NMR spectroscopy, were we able to assign completely the signals in the ^1H and ^{13}C NMR spectra of 1,1-dichloro-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene.[7]



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In the present work, we continued these studies and investigated the electron density distribution in substituted tetraphenylgermoles **1** ($R^1 = R^2 = H$, Me, *cyclo*-C_3H_5, $SiMe_3$, $SnMe_3$, $R^1 = Me$, $R^2 = H$, Cl) by NMR spectroscopy.

According to the C_2 symmetry of the molecules of germoles **1**, their ^{13}C NMR spectra contain ten signals corresponding to the carbon atoms of the heterocycle and to the phenyl groups of two nonequivalent types. In this case, the most complicated task is to identify the signals corresponding to the four quaternary carbon atoms, α-C, β-C, α-C_{ipso}, and β-C_{ipso}.

To assign these signals correctly, we took into account the fact that this part of the carbon spectrum contains two groups of signals (five signals each) that correspond to the four nonequivalent carbon atoms in the phenyl substituents (C_{ipso}, C_o, C_m, and C_p) and to the carbon atom of the ring attached to this phenyl group, α-C (α-C_{ipso}—) or β-C (β-C_{ipso}—). Thus, each group of atoms, α-C—α-Ph or β-C—β-Ph, is characterized by internal proton—proton and proton—carbon spin-spin coupling constants.

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Table 1. δ ^{1}H and δ ^{13}C chemical shifts for germoles **1** (a 10% solution in $CDCl_3$)

R^1	R^2	α-C	β-C	δ ^{13}C								δ ^{1}H					
				C_{ipso}		C_o		C_m		C_p		H_o		H_m		H_p	
				α	β	α	β	α	β	α	β	α	β	α	β	α	β
Cl	Cl	132.68	149.92	134.62	136.53	129.51	129.46	128.34	128.04	127.66	127.45	7.15	6.85	7.17	7.07	7.18	7.08
Cl	Me	137.39	151.72	137.48	137.90	129.16	129.74	128.14	127.72	126.63	126.77	7.05	6.83	7.13	7.02	7.10	7.05
H	H	139.18	153.79	139.54	139.21	129.54	129.68	127.96	127.65	126.12	126.40	7.00	6.85	7.13	7.05	7.08	7.06
Me	H	141.33	152.41	139.87	139.27	129.25	129.90	127.93	127.52	125.80	126.18	6.97	6.84	7.13	7.03	7.07	7.04
Me	Me	143.88	151.20	140.31	139.41	128.87	130.12	127.88	127.41	125.51	125.99	6.93	6.83	7.12	7.01	7.06	7.02
cyclo-C_3H_5	*cyclo*-C_3H_5	141.07	152.51	140.72	139.33	128.99	130.07	127.74	127.40	125.44	125.97	6.87	6.66	6.96	6.85	6.89	6.86
$SnMe_3$	$SnMe_3$	149.80	150.95	141.43	140.19	129.38	130.58	127.75	127.37	125.29	125.77	6.84	6.84	7.06	6.99	7.00	7.00
$SiMe_3$	$SiMe_3$	149.31	151.57	142.37	140.30	129.51	130.58	127.55	127.19	124.91	125.54	6.88	6.81	7.07	6.97	7.00	7.09

Note that the magnitudes of the vicinal proton—carbon constants are markedly larger than those of geminal constants. Therefore, spin-spin coupling over three covalent bonds (α-C_{ipso}—α-C_o—α-C_m—α-H_m) rather than coupling over two bonds (α-C_{ipso}—α-C_o—α-H_o) is manifested in the 2D spectra for the carbon atoms of the ring (for example, for α-C_{ipso}).

Using the standard 2D NMR techniques, *viz.*, NOEDIFF, COLOC, COSY, and XHCORRD, included in the software package for Bruker NMR spectrometers and the prospects for 2D spectroscopy that we described previously for 1,1-dichlorogermole,[7] we determined the exact chemical shifts for all the hydrogen and carbon atoms in the compounds under consideration.

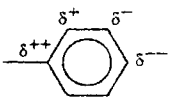
The resonance of the *ortho*-protons of the phenyl group located in the α-position of the heterocycle α-H_o served as the "starting point" in determining the partners in the spin-spin coupling. The position of this signal in the spectrum was determined using the nuclear Overhauser effect (NOE) resulting from the through-space interaction with the hydrogen atoms of the R^1 and R^2 substituents. Knowing the position of the signal for the α-^1H_o protons, one can find the chemical shifts for the other signals corresponding to the α-C—α-Ph fragment in the ^{1}H and ^{13}C NMR spectra.

Since the signals of the carbon atoms located in the *para*-positions can be easily identified, and the resonance of the α-C_p atom is already known, the second β-C_p signal can serve as the starting point for determination of the chemical shifts of the rest of the signals corresponding to the β-C—β-Ph fragment.

Results and Discussion

The ^{1}H and ^{13}C chemical shifts observed in the spectra of germoles **1** are listed in Table 1. They differ markedly from the values reported previously. For example, of the chemical shifts reported[5] for the four quaternary carbon atoms in 1,1-dimethylgermole, only the value for the β-C atom was correct. In the same study, the chemical shifts for all the quaternary carbon atoms (both in the ring and in the phenyl groups) of 1,1-bis(trimethylsilyl)germole were assigned incorrectly. For example, the highest-field signal (140.32 ppm) was attributed to the α-C atom adjacent to the germanium atom, whereas, in reality, this atom is responsible for the lowest-field signal at 151.52 ppm.

Analysis of the ^{13}C NMR spectra indicates that as the electron-donating ability of the R^1 and R^2 substituents increases, *i.e.*, in the sequence Cl, Cl → Cl, Me → H, H → H, Me → Me, Me → *cyclo*-(C_3H_5), *cyclo*-(C_3H_5) → ($SiMe_3$), ($SiMe_3$) → ($SnMe_3$), ($SnMe_3$), the chemical shift of the α-C carbon atom incorporated in the ring next to germanium increases monotonically from 132.68 ppm to 149.80 ppm, while shielding of the β-C atom remains virtually constant (151.9±2.0 ppm). The chemical shifts of the C atoms of the phenyl substituents both in the α- and β-positions also vary monotonically in this series of compounds (see Table 1). Whereas the values for the *ipso*- and *ortho*-carbon atoms increase (like those for the α-C atoms but to a lesser extent), the chemical shifts for *meta*- and *para*-carbon atoms decrease (Table 2). The fact that the ^{13}C Δδ values, *e.g.*, for α-C_{ipso} and α-C_p atoms, vary over substantially wider ranges (+9.7 and −3.0 ppm) than those for the α-C_o and α-C_m atoms (+0.7 and −0.9 ppm) indicates that there are no resonance effects or polarization of the phenyl groups. Otherwise, the ^{13}C Δδ values for the neighboring carbon atoms would alternate.[8]



The chemical shifts of the α-C_{ipso} and α-C_p atoms are related to each other by a good linear dependence:

$$\delta(\alpha\text{-}^{13}C_p) = 175.59 - 0.356 \cdot \delta(\alpha\text{-}^{13}C_{ipso}),\quad r = 0.988,\ n = 8,$$

$$\delta(\beta\text{-}^{13}C_p) = 193.37 - 0.483 \cdot \delta(\beta\text{-}^{13}C_{ipso}),\quad r = 0.962,\ n = 8.$$

Table 2. Ranges of variation of chemical shifts Δδ ^{1}H and Δδ ^{13}C for germoles **1** upon variation of substituents R^1 and R^2

Position	Δδ						
	C_{ipso}	C_o	C_m	C_p	H_o	H_m	H_m
α	9.7	0.7	0.9	3.0	0.27	0.10	0.18
β	3.8	1.2	0.9	2.0	0.04	0.10	0.09

This makes it possible to assume that the effects of the electronegativities of the R^1 and R^2 substituents on the phenyl groups in germoles **1** are manifested due to polarization of multiple bonds ("field effect") rather than being transferred through covalent bonds.

As a rule, ^{13}C NMR chemical shifts do not correlate with electron density, since the main contribution to the shielding is made by the paramagnetic constituent, which depends appreciably on structural changes.[9] However, in a series of compounds having similar structures, this contribution remains constant and its influence on the change in the shielding of a carbon atom decreases.[10] As a result, the effect of remote substituents is significant. For compounds having similar structures, the local change in the paramagnetic contribution to the shielding of carbon atoms can be attributed to redistribution of electron density caused by remote substituents. In these cases, ^{13}C NMR spectroscopy provides some information on the electronic structures of compounds. This approach has proved itself in a study of monosubstituted benzene derivatives. It was shown that the calculated charges for the σ- and π-populations of the *para*-carbon atom correlate well with its chemical shift.[11]

Therefore, we studied the correlation between the chemical shifts of the carbon atoms in germoles **1** and various constants of the substituents R^1 and R^2. The best correlation was observed between the chemical shift of the α-C_{ipso} carbon atom and the sum of the σ^* Taft constants for R^1 and R^2, which characterizes the electron-withdrawing capacity of the substituents transferred along the aliphatic chain.[12] The data for germole **1** with $R^1 = R^2 = SnMe_3$ were not included in the correlation, because there is no reliable σ^* value for this substituent:[13]

$$\delta(\alpha\text{-}C_{ipso}) = 140.535 - 1.039 \cdot \Sigma\delta^*, \quad r = 0.997, \quad n = 7;$$
$$\delta(\beta\text{-}C_{ipso}) = 139.468 - 0.509 \cdot \Sigma\delta^*, \quad r = 0.992, \quad n = 7;$$
$$\delta(\alpha\text{-}C_p) = 125.577 - 0.373 \cdot \Sigma\delta^*, \quad r = 0.994, \quad n = 7;$$
$$\delta(\beta\text{-}C_p) = 126.017 - 0.257 \cdot \Sigma\delta^*, \quad r = 0.993, \quad n = 7.$$

The shielding of all the aromatic protons in the α- and β-phenyl groups regularly increases over the series of compounds from dichloro- to bis(trimethylsilyl)-substituted germole (see Table 1). For all the compounds studied, the signal for the *ortho*-protons of the phenyl groups occupying the β-positions experiences the smallest shifts and is always the highest-field signal in the spectrum (6.83±0.02 ppm). Conversely, the shielding of the *ortho*-protons in the α-phenyl groups changes substantially (from 7.15 to 6.88 ppm). As a whole, the changes in the chemical shifts of the protons of the phenyl groups in the α-positions are markedly larger than those for the β-phenyl groups (see Table 2).

The above-discussed variations of the ^{13}C chemical shifts in the series of germoles **1** indicate that the effects of the substituents R^1 and R^2 on the heterocycle and on the benzene rings are inductive rather than mesomeric effects and that the direct through-space transfer (field effect) is also significant.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 300.13 and 75.45 MHz, respectively. The ^{13}C chemical shifts were measured in relation to the signal of chloroform (77.00 ppm). Standard 2D NMR spectroscopy techniques, COLOC, COSY and XHCORRD, were used in the study.

The samples of germoles were synthesized by known procedures.[14–18]

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