trated, and analyzed by GLC and ^{1}H NMR spectroscopy using 1,4-dichlorobenzene as the internal standard.

To construct the curves for the accumulation of electrolysis products (see Figs. 1 and 2), small portions of the reaction mixture were withdrawn at regular intervals during the electrolysis and analyzed by GLC and ^{1}H NMR spectroscopy.

Tetramethyl 1,1,2,2-ethanetetracarboxylate 2a,[2] m.p. 136—137 °C. ^{1}H NMR, δ: 3.76 (s, 12 H, CH_3O), 4.14 (s, 2 H, CH). ^{13}C NMR, δ: 51.1 (d, CH), 52.9 (q, CH_3O), 167.3 (s, C=O).

Tetramethyl ethenetetracarboxylate 3a,[3] m.p. 119—120 °C. ^{1}H NMR, δ: 3.85 (s, 12 H, CH_3O). ^{13}C NMR, δ: 53.2 (q, CH_3O), 135.2 (s, C=C), 162.5 (s, C=O).

Tetraethyl ethylenetetracarboxylate 3b,[3] m.p. 55—56 °C. ^{1}H NMR, δ: 1.35 (t, 12 H, CH_3), 4.29 (q, 8 H, CH_2O). ^{13}C NMR, δ: 13.5 (q, CH_3), 62.1 (t, CH_2O), 135.3 (s, C=C), 162.2 (s, C=O).

Tetramethyl methoxyethane-1,1,2,2-tetracarboxylate 4a,[3] m.p. 54—56 °C (ether—pentane). ^{1}H NMR, δ: 3.54 (s, 3 H, CH_3O), 3.74 and 3.84 (both s, 12 H, CO_2CH_3), 4.23 (s, 1 H, CH). ^{13}C NMR, δ: 52.1, 52.3, and 55.0 (all q, CH_3O), 52.7 (d, CH), 83.9 (s, C—OMe), 165.4 and 166.9 (both s, C=O).

Hexamethyl propane-1,1,2,2,3,3-hexanecarboxylate 5a,[4] m.p. 136—137 °C. ^{1}H NMR, δ: 3.76 (s, 12 H, CH_3O), 3.79 (s, 6 H, CH_3O), 4.27 (s, 2 H, CH). ^{13}C NMR, δ: 52.6 and 53.0 (both q, CH_3O), 54.1 (d, CH), 58.9 (s, C), 167.3 and 167.9 (both s, C=O).

Hexaethyl propane-1,1,2,2,3,3-hexanecarboxylate 5b,[4] b.p. 184—186 °C (0.25 mm), m.p. 40—42 °C (ether—pentane). ^{1}H NMR, δ: 1.26 and 1.28 (both t, 18 H, CH_3), 4.23 (q, 8 H, CH_2O), 4.25 (s, 2 H, CH), 4.26 (q, 4 H, CH_2O). ^{13}C NMR, δ: 13.3 and 13.5 (both q, CH_3), 54.2 (d, CH), 58.5 (s, C), 61.4 and 61.9 (both t, CH_2O), 166.8 and 167.2 (both s, C=O).

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Correlation NMR spectroscopy of 1,1-dichloro-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene

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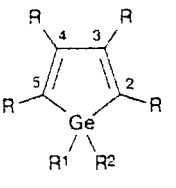
Assignment of all of the signals in the ^{1}H and ^{13}C NMR spectra of 1,1-dichloro-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene has been carried out using two-dimensional NMR spectroscopy.

Key words: germanium, 1-germacyclopenta-2,4-diene, ^{13}C and ^{1}H NMR spectroscopy.

1-Germacyclopenta-2,4-dienes (germoles) constitute an interesting class of organogermanium heteroaromatic compounds. However, they have been studied less extensively[1,2] than siloles, phospholes and much less extensively than pyrroles, furans, and thiophenes. The stability of germoles in the monomeric form, like that of siloles, markedly increases when alkyl or aryl substituents are introduced into the ring;[1,2] therefore, substituted metaloles are convenient objects for studying their structures by physicochemical methods. From the synthetic viewpoint, stable 2,3,4,5-tetraphenylgermoles (**1**, R = Ph) are the most accessible.



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These compounds are easily prepared[1] by the reaction of the dilithium salt of tetraphenylbutadiene with the corresponding dichloride $R^1R^2GeCl_2$.

Therefore, it is no wonder that germoles **1** (R = Ph) have become popular objects of studies including studies carried out by physicochemical methods.[1,2]

The results of NMR studies of germoles are fragmentary.[1] Data on the ^{13}C NMR spectra of 2,3,4,5-tetraphenylgermoles have been reported only recently.[3,4] However, the assignment of the signals of the carbon atoms of the germacyclopentadiene moiety and of the phenyl groups have proven to be rather complicated. For example, the two signals in the lowest field in the ^{13}C NMR spectra of tetraphenylgermoles **1** (R = Ph; $R^1 = R^2 = Cl$, Me, $Bu^tC{\equiv}C$; $R^1 = Cl$, $R^2 = FeCp(CO)_2$; $R^1 = Cl$, $R^2 = WCp(CO)_3$) studied in Ref. 4 were attributed to the heterocyclic carbon atoms without indication of which of these signals corresponds to the C(2) and C(5) (α-C) atoms and which signal relates to C(3) and C(4) (β-C). The authors were also unable to distinguish between the signals of *ipso*-, *ortho*-, *meta*-, and *para*-carbon atoms in the phenyl substituents in the α- and β-positions.

In order to precisely assign the ^1H and ^{13}C NMR signals of germoles **1**, we studied dichlorogermole **1a** (R = Ph; $R^1 = R^2 = Cl$) as a model compound by two-dimensional NMR spectroscopy. To achieve correct assignment of the signals, we took into account the fact that the aromatic part of the carbon spectrum should consist of signals from two groups of atoms: α-C—Ph-α and β-C—Ph-β; internal proton—proton and proton—carbon spin-spin coupling constants should be manifested in both of them.

To determine the partners in the spin-spin coupling, the signal of the β-C atom was chosen as the "starting point". It is known that the signals for the β-C atoms of the germacyclopentadiene fragment of tetramethylgermoles **1** (R = Me) are located downfield of those for the α-C atoms, *viz.*, at 145 and 132 ppm ($R^1 = R^2 =$ Me, in acetone)[5] and at 147 and 125 ppm ($R^1 = R^2 =$ Cl, in THF), respectively.[6] This characteristic feature has also been observed for siloles of a similar structure (R = Me, Ph).[7,8] According to the ^{13}C NMR spectroscopy data, the lowest-field signals in the spectra of germoles **1** containing organic substituents at the germanium atom[3,4] is exhibited in the narrow range, δ 151 ± 1. Therefore, the first signal of the four signals (149.92, 136.53, 134.62, and 132.68 ppm) corresponding to α-C, β-C, α-C_{ipso}, and β-C_{ipso} in the ^{13}C NMR spectrum ($CDCl_3$, 20 °C) of compound **1a** belongs to the β-C carbon atom. The other signals are shifted markedly upfield and are manifested in the region typical of phenyl groups (137—132 ppm).

The β-C carbon atom of the ring (as well as the α-C atom) has vicinal spin-spin coupling constants with the two *ortho*-protons of the Ph ring attached to it, owing to coupling along the β-C—β-C_{ipso}—β-C_o—β-H_o chain. To record cross-peaks at small values of spin-spin coupling constants (1—3 Hz), we used the standard COLOC sequence optimized for this particular case. An experiment carried out in $CDCl_3$ showed that the signal at 149.92 ppm (β-C) in the 2D spectrum has a cross-peak with the phenyl-group protons at 6.85 ppm. In the ^1H NMR spectrum, this isolated multiplet corresponds to the *ortho*-protons of the phenyl groups attached to the β-carbon atoms (β-H_o). For the β-H_o protons, a cross-peak with the carbon atom in the *para*-position, β-C_p, is observed, owing to the vicinal coupling along the β-H_o—β-C_o—β-C_m—β-C_p chain. Based on the foregoing, the signal at 127.45 ppm can be assigned to the β-C_p carbon atom.

Using the 2D homonuclear correlation technique (COSY), it was found that the signal corresponding to the β-H_o has a cross-peak in the region of 7.07 ppm, due to of vicinal coupling H—C—C—H with the *meta*-protons (β-H_m). For β-H_m, a cross-peak is also recorded at 136.53 ppm in the COLOC spectrum; it results from vicinal coupling (β-H_m—β-C_m—β-C_o—β-C_{ipso}) with the β-C_{ipso} carbon atom. Thus, the precise assignment of the signal for the β-C_{ipso} carbon atom was accomplished using the following sequence of 2D spectra:

$$\beta\text{-C} \xrightarrow{\text{COLOC}} \beta\text{-H}_o \xrightarrow{\text{COSY}} \beta\text{-H}_m \xrightarrow{\text{COLOC}} \beta\text{-C}_{ipso}$$

Since in the spectrum recorded in $CDCl_3$, the chemical shifts of the *ortho*-, *meta*-, and *para*-protons of the phenyl substituents attached to the α-C carbon atoms virtually coincide (their signal is a broadened singlet at 7.17 ppm), it is impossible to carry out a similar analysis for the α-C—Ph fragment. To observe the signals from these protons separately, we used an anisotropic solvent, benzene. The replacement of the solvent changes the chemical shifts of the protons but has almost no effect on the chemical shifts of the carbon atoms (Table 1).

The position of the signal due to α-C_p in the spectrum of α-C—Ph is easy to determine. Since the chemical shift of the β-C_p atom is already known (127.45 ppm in $CDCl_3$), the second signal located downfield, at 127.66 ppm (or at 128.14 ppm in benzene) corresponds to the α-C_p atoms.

Thus, using 2D spectra, we determined the exact values of the chemical shifts of the protons and carbon atoms (the chemical shifts in C_6D_6, ppm, are given in parentheses):

$$\alpha\text{-C}_p\,(128.14) \xrightarrow{\text{COLOC}} \alpha\text{-H}_m\,(6.95) \xrightarrow{\text{COSY}} \alpha\text{-H}_0\,(7.42) \longrightarrow$$

$$\xrightarrow{\text{COLOC}} \alpha\text{-C}\,(133.41)$$

The signals of the α-C_o and α-C_m atoms were assigned using $^1H—^{13}C$ correlation spectroscopy for direct spin-spin coupling constants (XHCORRD).

The one-dimensional ^1H NMR spectrum of dichlorogermole **1a** is so complicated that even the COSY

Table 1. Assignment of signals in the ^1H and ^{13}C NMR spectra of 1,1-dichloro-2,3,4,5-tetraphenylgermole **1a** (δ)

Atom	Position	Solvent			
		$CDCl_3$	C_6D_6	$CDCl_3$ [3]	$CDCl_3$ [4]
α-C		132.68	133.41	132.76	
β-C		149.92	150.56	149.99	136.7, 150.1
C_{ipso}	α	134.62	135.22	134.69	
	β	136.53	137.05	136.59	131.6, 134.8
C_o	α	129.51	129.97	129.51	
	β	129.46	129.85	129.59	129.6, 129.6
C_m	α	128.34	128.86	128.37	
	β	128.04	128.23	128.08	128.1, 128.4
C_p	α	127.66	128.14	127.47	
	β	127.45	127.60	127.71	127.5, 127.7
H_o	α	7.15	7.42		
	β	6.85	6.66		
H_m	α	7.17	6.95		
	β	7.07	6.77		
H_p	α	7.18	6.88		
	β	7.08	6.76		

spectrum does not permit one to attribute signals to particular protons. Only analysis of the XHCORRD spectrum made it possible to assign precisely the signals of the *ortho*-, *meta*-, and *para*-protons over the markedly narrower range of variation of the ^1H NMR chemical shifts of the phenyl substituents (less than 3 ppm) using the well resolved cross-peaks (see Table 1).

Thus, using 2D NMR spectroscopy techniques, we determined for the first time the exact values of the chemical shifts of all the carbon and hydrogen atoms in the molecule of dichlorogermole **1a**.

Experimental

^1H and ^{13}C NMR spectra of germole **1a** were recorded on a Bruker AM-300 spectrometer (operating at 300.13 and 75.45 MHz, respectively). The ^1H and ^{13}C chemical shifts were measured in relation to internal $CDCl_3$ (7.27 and 77.00 ppm) and C_6D_6 (7.38 and 127.00 ppm). Standard 2D NMR spectroscopy techniques (COLOC, COSY and XHCORRD) were used.

This sample of dichlorogermole **1a** was synthesized by the known procedure.[9]

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