COMPLETE ANALYSIS OF THE AA'BB' NMR-^{1}H SPECTRUM OF 1, 1, 1, 3-TETRACHLOROPROPANE BY METHODS OF HETERO- AND HOMONUCLEAR DOUBLE RESONANCE

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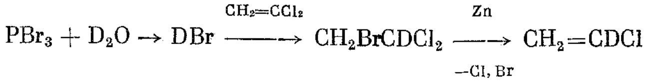
In a study of the stereochemistry of the telomerization of vinyl chlorides with polyhalomethanes by conformational NMR analysis of the telomer homologs $CCl_3(CH_2CHCl)_n X$ (where X = Cl, Br, H, n = 1-3), the possibility of evaluating the conformational state of nonsymmetrical* long-chain aliphatic hydrocarbons according to individual molecular fragments was discovered. One of the fragments most widespread in the investigated polyhaloalkane molecules is the fragment $R_2CClCH_2CH_2Cl$, a complete analysis of the proton spectrum of which (with 1, 1, 1, 3-tetrachloropropane as an example) is cited in the present communication.

This spectrum (Fig. 1) contains two groups of 11 lines, symmetrical with respect to the center, and belongs to the type AA'BB', characteristic [2-5] of 1, 2-disubstituted ethanes.† An analysis of such spectra is associated with definite difficulties [5-12], and an unambiguous solution is possible only using supplementary experimental methods [6-8]. Thus, in [6] a method of direct evaluation of all the parameters of the spectrum AA'BB' according to the data for several working frequencies of the spectrometer was proposed. The authors of [7] conducted a primary assignment of the lines by the INDOR method. In [8], reliable values for the geminal constants in 1, 2-chlorobromoethane were successfully obtained by a consideration of two-quantum transitions. We used selective deuteration, variation of the working frequency, and double resonance – observation of the Overhauser effect by the INDOR method and uncoupling of the ^{1}H-nuclei from spin–spin interaction with the deuteron.

METHOD

T_1^H was synthesized by telomerization of vinyl chloride with chloroform according to the method of [13]; 1, 1, 1, 3-tetrachloro-3-d_1-propane (T_1^D) was synthesized by telomerization of α-d_1-vinyl chloride with $CHCl_3$. The deutero-analog T_1^D had bp 41° (0.2 mm) and n_D^{20} 1.4814. Found: C 20,10; D + H 2.43; Cl 77.24%. CCl_3CH_2CHDCl. Calculated: C 19.69; H + D 2.73; Cl 77.58%. α-T_1-Vinyl chloride was produced in three steps:



$$PBr_3 + D_2O \rightarrow DBr \xrightarrow{CH_2=CCl_2} CH_2BrCDCl_2 \xrightarrow[-Cl,\,Br]{Zn} CH_2=CDCl$$

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* According to the nomenclature of [1], molecules that do not have any elements of symmetry other than the trivial axis C_1 are called nonsymmetrical or asymmetrical.

† In conformational NMR analysis, 1, 1, 1, 3-tetrachloropropane (T_1^H) can be considered as a 1, 2-disubstituted ethane, since the magnetically inactive group CCl_3 possesses symmetry C_{3v}, and rotation around the C_1-C_2 bonds does not change the shielding constant of the neighboring protons or the conformational composition of the remainder of the molecule.

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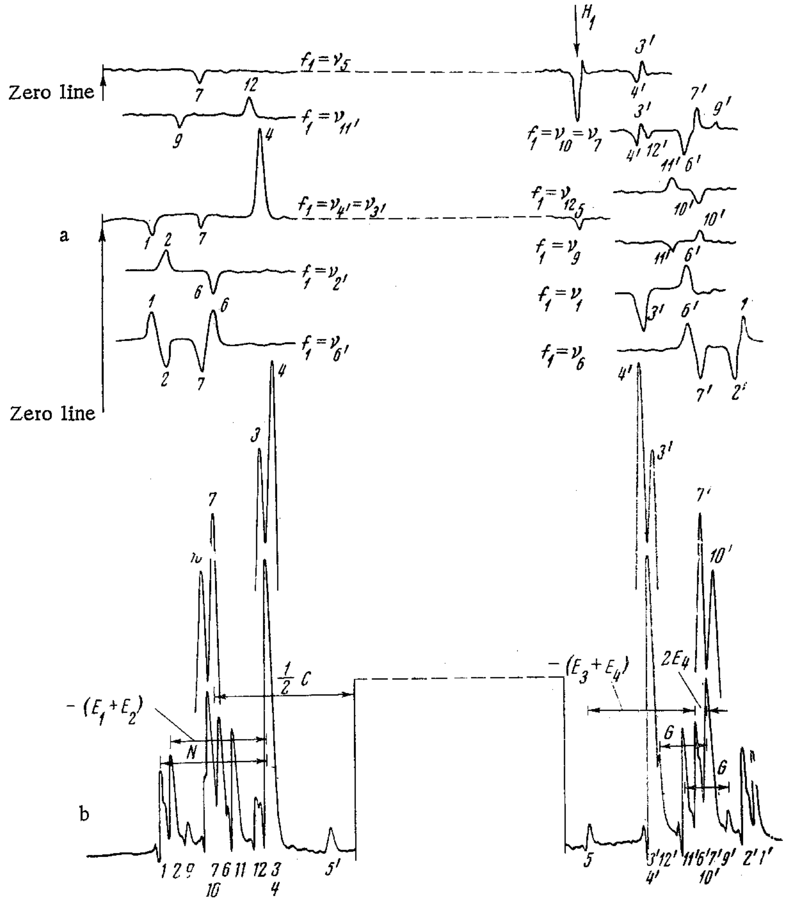

Fig. 1. NMR-^{1}H spectra and INDOR of 1,1,1,3-tetrachloropropane at the frequency 60 MHz (50 vol.% in benzene): a) INDOR experiments; b) NMR-^{1}H experiments. Calculation of the spectrum by the method of [9] was performed according to the indicated intervals (the roots E_1-E_4 of E_2 8.184 in [5]).

The addition of DBr to vinylidene chloride was performed, in contrast to [14],* at 80° in sealed glass ampoules with a volume of 50 ml with 0.02 g benzoyl peroxide, 40 g $C_2H_2Cl_2$, and 25 g DBr (mole ratio $[DBr]/[C_2H_2Cl_2] = 0.75$). Before the experiment the monomer was redistilled in a stream of dry purified argon. Each reagent, after introduction into the ampoule, was treated twice with a cycle of freezing–evacuation–thawing. In 3 h, an adduct containing < 1% high-boiling impurities was obtained with a quantitative yield and 97% conversion of DBr. After washing with a 5% solution of Na_2CO_3, with water, and drying, the fraction with bp 135-136°; d_4^{20} 1.7650 and n_D^{20} 1.5125 was distilled off. The NMR-^{1}H spectrum of $CH_2BrCDCl_2$ contained a triplet with splitting $J_{HD} \sim 0.9$ Hz in the region of absorption of the protons of the CH_2Br group of the light analog at 3.86 ppm ($J_{HD} \sim 6.5$ Hz).

The method of dehalogenation did not differ from that described in [14, 15]. The yield of α-d_1-vinyl chloride at this stage was 89 or 70% of the initial D_2O, the content of $CH_2{=}CHCl \sim 4\%$ (Fig. 2), with isotopic purity of $D_2O < 97\%$. All the parameters determined from the spectrum of the deutero-analog: $\Delta\nu_{AB} = 5.0$; $J_{AB} = 1.4$; $J_{AC} = J_{AD} \cdot 6.51 = 7.2$; $J_{BC} = J_{BD} \cdot 6.51 = 15.1$ Hz, practically coincided with the data of [16] of a calculation of the spectrum of vinyl chloride in the ABC approximation (5.4, 1.5, 6.8, and 14.8 Hz, respectively).

The NMR-^{1}H spectra of T_1^H and T_1^D were taken at the frequency 90 MHz (34°, Brüker HX-90 spectrometer) and 60 MHz (34°, Hitachi–Perkin–Elmer R-20 spectrometer). The ampoules with the substance to

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* The authors of [14] initiated the addition of DBr to $CH_2{=}CCl_2$ with UV irradiation. After 18 h at 25°, the yield of the adduct was 62% (bp 134-135°, n_D^{25} 1.5054).

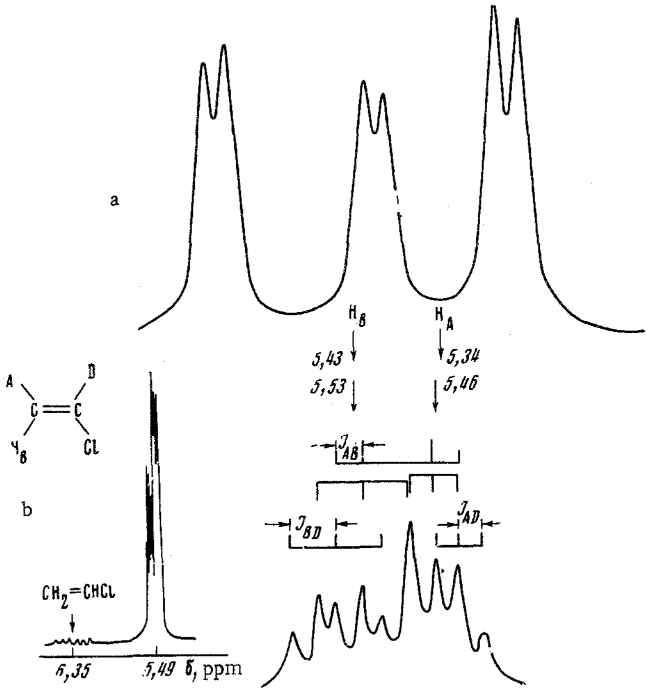

Fig. 2. PMR spectra of vinyl chloride (a) and α-d_1-vinyl chloride (b), 60 MHz, ~ 34°, 40% in CCl_4, standard TMS.

be analyzed were purged with argon, then evacuated at −76° and sealed. The intervals between the lines were determined by averaging no less than three spectra. The standard error of the determination of the spin–spin interaction constants did not exceed 0.05 Hz, that of the chemical shifts 0.002 ppm.

The INDOR experiment was conducted on a modernized RYa-2305 spectrometer (25°) with frequency development. The reference signal during internal stabilization was the line of benzene. The fixed frequency of modulation f_3 was 1 kHz. The modulation frequencies of the measuring f_1 and perturbing f_2 fields were measured with an accuracy of 0.1 Hz.

Complete uncoupling of the spins of the ^1H nuclei from D was observed in the irradiation of the latter with a saturating field H_2 with frequency 9.213310 MHz (RYa-2305). The splittings on the deuteron permitted calibration of H_2. The value of the field in experiments on T_1^D reached 1800 Hz, which caused heating of the sample to ~ 50°. Moreover, experiments were conducted with noise suppression [17, 18] by phase modulation of H_2 from a generator of a quasi-random sequence of pulses. Complete uncoupling at an

TABLE 1. Parameters of the Proton Spectrum AA'BB' of 1, 1, 1, 3-Tetrachloropropane (Hz)

Solvent	Concentration of T_1^H, vol.%	$\Delta\nu_{AB}$	K	L	M	N	$J_{AA'}$ $ClCH_2$	$J_{BB'}$ CCl_3CH_2	J_{AB}	$J_{AB'}$	δ_B, ppm	δ_A, ppm
d_8-Toluene	20	40,00	−25,15	5,92	3,49	15,70	−10,84	−14,32	4,89	10,82	2,409	3,741
" *	20	60,02	−25,06	5,83	3,60	15,69	−10,73	−14,33	4,93	10,75	2,410	3,740
Benzene	20	39,32	−25,07	5,72	3,47	15,64	−10,80	−14,27	4,96	10,68	2,822	3,478
"	50	39,18	−25,12	6,02	3,42	15,74	−10,85	−14,27	4,95	10,79	2,824	3,476
CCl_4	50	38,10	−24,87	6,19	3,55	15,89	−10,66	−14,21	4,85	11,04	3,133	3,767
" †	50	38,8	—	—	—	—	−10,7	—	6,0	9,0	3,15	3,80
Benzene ‡	50	72,58	−25,19	5,19	3,73	15,41	−10,73	−14,46	5,11	10,30	2,241	3,451
" **	50	70,62	−25,19	5,05	3,65	15,63	−10,77	−14,43	5,30	10,34	2,354	3,530

* The spectrum was taken at a frequency of 90 MHz.

† The parameters were determined from the spectrum of the deutero-analog of T_1^D.

‡ Compound $ClCH_2CH_2CCl_2CH_2CH_2Cl$.

**Compound $ClCH_2CH_2CCl_2CH_3$.

amplitude of the perturbing field of 1800 Hz occurred with a frequency difference of ± 2.5 kHz. The frequency H_2 was set by a frequency synthesizer, started by the quartz generator of the spectrometer (5 MHz).

The parameters of the spectrum (Table 1) were determined on a Minsk-22 electronic computer according to an iteration program. The standard deviations from the experimental values of the frequencies calculated according to these parameters were 0.06 Hz, i.e., were close to the experimental error.

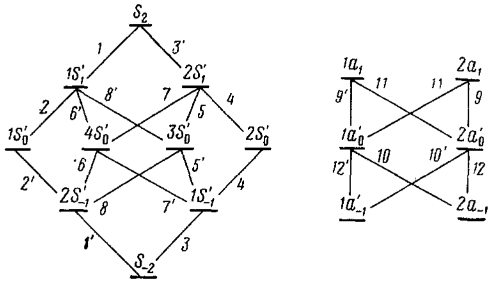

Fig.3. Energy diagram of the four-spin system AA'BB' [7, 9, 12]. The numbers of the transitions correspond to those indicated in Fig.1.

RESULTS AND DISCUSSION

For a description of the AA'BB' spectrum of T_1^H, it is necessary [5, 9, 10, 12] to find the differences in the chemical shifts $\Delta\nu_{AB} = \nu_A - \nu_B$ and values of four parameters: $K = \pm|J_{AA'} + J_{BB'}|$, $M = |J_{AA'} - J_{BB'}|$, $N = |J_{AB} + J_{AB'}|$, $L = |J_{AB} - J_{AB'}|$, where $J_{AA'}$ and $J_{BB'}$ are the geminal, J_{AB} and $J_{AB'}$ the rotationally averaged vicinal spin–spin interaction constants. Since the spectrum does not permit a distinguishment of $J_{AA'}$ from $J_{BB'}$ or J_{AB} from $J_{AB'}$ (i.e., an assignment of the constants to individual pairs of nuclei), the solution of the reverse problem – estimation of the parameters of the spectrum according to the experimental frequencies – cannot establish the signs of M, N, and L [10, 11]. However, the shape of the spectrum AA'BB' is sensitive to the relative signs of K and N [10], which makes it possible to determine the signs of the geminal and vicinal constants.

As can be seen from Fig.1, in the spectrum of T_1^H, individual lines correspond to almost all the basic transitions permitted for the system AA'BB' [5]. They were preliminarily assigned by the INDOR method [18, 19]. Some results of the INDOR experiment are presented in Fig.1. The symmetry of the spectrum AA'BB' permitted observation of the lines of one group under the action of a perturbing field on the transitions of the other. The shape of the energy diagram for a four-spin system of two pairs of chemically equivalent nuclei is indicated in Fig.3 [7, 9, 12].

In accord with the diagram in the case of fixation of the frequency f_1 of the measuring field H_1 according to the maximum of the line 1 ($f_1 = \nu_1$), we obtain a positive signal at $f_2 = \nu_6$, and a negative signal at $f_2 = \nu_3$, (the result for $f_1 = \nu_6$, is symmetrical). A positive signal ν_2, and a negative signal ν_6, corresponds to the transition 2; a negative $\nu_{2'}, \nu_{7'}$, and positive $\nu_{1'}, \nu_{6'}$ corresponds to transition 6 (the same for $f_1 = \nu_{6'}$, etc.). The transitions 9-12 between levels corresponding to the antisymmetrical spin function form an independent group of lines. Although the observation of the Overhauser effect permits an easy distinguishment of these lines in the spectrum AA'BB', assignment within the group on the basis of the INDOR experiment alone is impossible (for example, selection between the sequence 9-10-11-12 or 10-9-12-11).

Despite the insufficient sensitivity of the INDOR method [7], we succeeded in identifying the low-intensity line 5 and thereby determining the sign of K. When $f_1 = \nu_5$, a negative signal with $f_2 = \nu_7$ or $f_2 = \nu_{4'}$ and a positive signal for $f_2 = \nu_{3'}$ was observed (see Fig.1). The line 8 was not detected, but, as calculation showed, its intensity in the spectrum of T_1^H is 1.5 orders of magnitude lower than for the transition 5. Thus, the INDOR method permitted a simultaneous assignment of the lines 1-7 and isolation of the quartet 9-12. Calculation of the parameters was performed on an electronic computer, on the basis of the experimental frequencies, or by the method of [9] with resolution of the spectrum into four groups of characteristic intervals (see Fig.1). The results of the machine calculation are cited in Table 1. The parameters, determined according to [9], differed from the table data by an average of 0.06 Hz.

As can be seen from Table 1, the value of K lies within the usual limits for 1, 2-dihalosubstituted ethanes (from –20 to –30 Hz [3, 4, 8, 11]). The parameters $L \neq 0$, in accord with [20], for T_1^H, $J_{AB} \neq J_{AB'}$. The latter may mean that in the weakly polar solvents studied there is a rapid rotation around the $C_2 - C_3$ bond with different weights of the three energetically profitable rotamers.

The correctness of the assignments in Fig.1 and the calculation of the parameters is confirmed by the following methods. The spectrum at the frequency 90 MHz was described with an accuracy within the experimental error by the parameters K, L, M, and N, determined at the frequency 60 MHz (see Table 1).

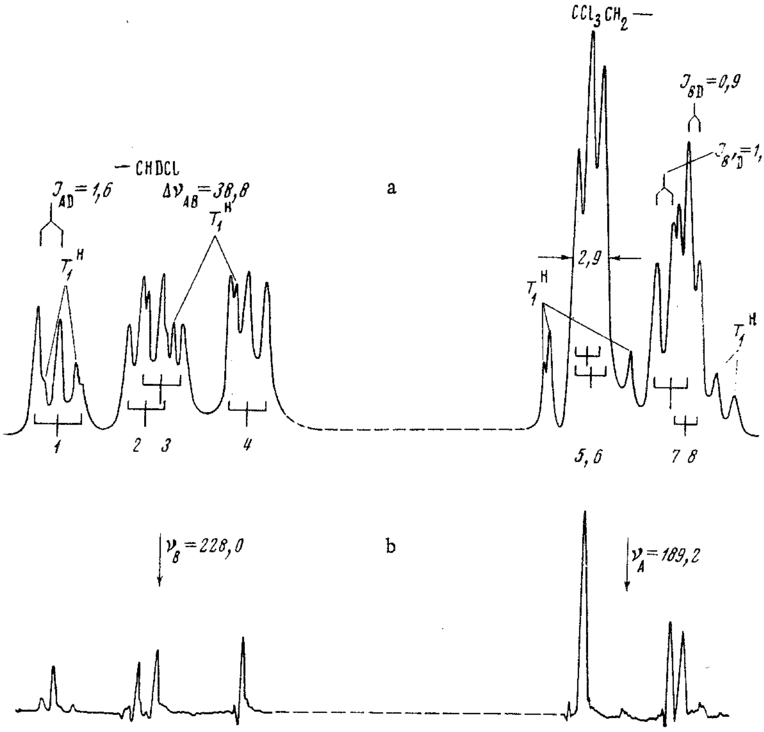

Fig. 4. NMR-^{1}H and INDOR spectra of 1, 1, 1, 3-tetrachloro-3-d_1-deuteropropane, 60 MHz, 50 vol.% in CCl_4, standard TMS: a) in the absence of suppression {D} (~ 34°). The assignment of eight basic ABB' transitions according to [5] is indicated; b) with complete uncoupling of ^1H-{D} (~ 25°).

Calculation with various combinations of signs of K and N led to a coincidence of the frequencies and intensities of the theoretical spectrum with the experiment and the observed position of the lines 5-7 only for $K < 0$ and $N > 0$. The variation of K even within narrow limits (± 3 Hz) was accompanied by a substantial shift of the signal 5 in the presence of constancy of the shape of the remainder of the spectrum. These data show that for T_1^H, like other 1, 2-disubstituted ethanes [2-5, 11], the geminal constants are opposite in sign to the vicinal constants, and according to [5, 8, 21], $J_{AA'}(J_{BB'}) < 0$ and $J_{AB}(J_{AB'}) > 0$. Moreover, from $|K| > |M|$ and $|N| > |L|$ it follows [10] that the signs of $J_{AA'}$, $J_{BB'}$ or J_{AB} and $J_{AB'}$ are the same.

The isotopic shift and uncoupling of the nuclei ^1H-{D} not only confirmed the analysis of the spectrum of T_1^H, but also permitted an unambiguous assignment of the subspectra of the CCl_3CH_2, $ClCH_2$ groups, i.e., a distinguishment of the geminal constants $J_{AA'}$, $J_{BB'}$. The spectrum of the deutero-analog T_1^D is shown in Fig. 4. The introduction of D converts the system AA'BB' of T_1^H to the relatively easily interpreted AXBB', and the three new constants for T_1^D—J_{AX}, J_{BX}, and $J_{B'X}$ are related [5] by simple functions to the geminal and vicinal constants of T_1^H: $J_{AA'} = J_{AX} \cdot 6.51$; $J_{A'B} = J_{BX} \cdot 6.51$.

The shape of the protonic spectrum ABB' of three nuclei, two of which in T_1^D are chemically equivalent, is determined only by the dimensionless ratio $\bar{J}_{AB}/\Delta\nu_{AB}$, where $\bar{J}_{AB} = (J_{AB} + J_{AB'})/2$ [5]. For T_1^D the value of $\bar{J}_{AB}/\Delta\nu_{AB} = 0.209$, taken from the spectrum of T_1^H, describes the observed picture with good accuracy. The deviations of the calculated frequencies of the eight basic ABB' transitions from the experiment did not exceed 0.15 Hz, and the low intensity line corresponding to the Raman transition 9 was actually detected at a calculated frequency of 77.8 Hz from ν_B (see Table 8.13 in [5]).

The isotopic shift appreciably increased the chemical shift $\Delta\nu_{AB}$* (see Table 1). From the triplet splitting on the deuteron of the signals from the protons of CCl_3CH_2, we obtained the vicinal constants in

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* According to the data of [22], the change in the chemical shift of the CH_2 group when the D atom is introduced is ≤ 0.4 Hz.

T_1^D, differing somewhat from those in T_1^H: $J_{AB} = 6.0 \pm 0.5$ and $J_{AB'} = 9.0 \pm 0.5$ Hz. However, the errors in the determination of the latter values are too large to judge the influence of the deuterium atom on the conformational equilibrium.

From an analogous splitting of the signal from the proton of the CHDCl group, we determined the value of the geminal constant $J_{AA'} = 10.7 \pm 0.4$ Hz, close to the calculated value (see Table 1), which proved comparable with the constant for the $ClCH_2$ group in 1, 2-chlorobromoethane (−9.9 Hz [8]), 1, 2-dichloropropane (−11.1 Hz [3]), 1-chloro-3,3-dimethylbutane (−10.5 Hz [23]), and in other 1-chloro-2-substituted ethanes (−10.6 to −11.8 Hz [11]). The value of $J_{AA'}$ for the assignment used in Figs. 1 and 4 gives a positive sign of M and a sequence of lines 9-12, indicated in Fig. 1.

In conclusion, let us note that the parameters of the proton spectrum of the fragment $R_2ClCCH_2CH_2Cl$ in compounds with R = Cl and Alk practically coincided with those observed for T_1^H, despite the almost doubling of $\Delta\nu_{AB}$. The corresponding values calculated according to the method of [9] for $ClCH_2CH_2CCl_2 \cdot CH_2CH_2Cl$ and $ClCH_2CH_2CCl_2CH_3$ are cited in Table 1.

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CONCLUSIONS

1. A complete analysis of the proton AA'BB' spectrum of 1, 1, 1, 3-tetrachloropropane was carried out by the methods of homo-(INDOR) and heteronuclear $^1H\{D\}$ double resonance, with an electronic-computer calculation of the spectra according to an iteration program for the two working frequencies 60 and 90 MHz.

2. Using the NMR-^{1}H spectrum of the deutero-analog 1, 1, 1, 3-tetrachloro-3-d_1-propane, the values of the geminal constants in the $ClCH_2$(−10.7 Hz) and CCl_3CH_2 groups (−14.4 Hz) were determined.

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