COMPLETE ANALYSIS OF THE AA'BB' NMR-^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 pro-
ton spectrum of which (with 1, 1, 1, 3-tetrachloropropane as an example) is cited in the present communica-
tion.

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 INDO 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 INDO method and uncoupling of the ^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_1D) was synthesized by telomerization of \(\alpha\)-d_1-vinyl chloride with
CHCl_3. The deuterio-analog T_1D had bp 41° (0.2 mm) and nD 1.4814. Found: C 20.10; D + H 2.43; Cl 77.24%.
CCl_3CH_2CDCl. Calculated: C 19.69; H + D 2.73; Cl 77.58%. \(\alpha\)-T_1-Vinyl chloride was produced in three
steps:

\[
PBr_3 + D_2O \rightarrow DBr \quad \rightarrow \quad CH_2BrCDCl_2 \quad \rightarrow \quad CH_2=CDCl
\]

* 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-disub-
stituted 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-1H spectra and INDO of 1,1,1,3-tetrachloropropane at the frequency 60 MHz (50 vol. % in benzene): a) INDO experiments; b) NMR-1H 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 \( \text{C}_2\text{H}_2\text{Cl}_2 \), and 25 g DBr (mole ratio \([\text{DBr}]/[\text{C}_2\text{H}_2\text{Cl}_2] = 0.75\). 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-evaporation-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 \( \text{Na}_2\text{CO}_3 \), with water, and drying, the fraction with \( \text{bp} \) 135-136°, \( d^2_2 \) 1.7650 and \( n^2_2 \) 1.5125 was distilled off. The NMR-1H spectrum of \( \text{CH}_2\text{BrCDCl}_2 \) contained a triplet with splitting \( J_{\text{HD}} \sim 0.9 \text{ Hz} \) in the region of absorption of the protons of the \( \text{CH}_2\text{Br} \) group at 3.86 ppm (\( J_{\text{HD}} \sim 6.5 \text{ Hz} \)).

The method of dehalogenation did not differ from that described in [14, 15]. The yield of \( \alpha-\text{d}_4\)-vinyl chloride at this stage was 89 or 70% of the initial \( \text{D}_2\text{O} \), the content of \( \text{CH}_2=\text{CHCl} \sim 4\% \) (Fig. 2), with isotopic purity of \( \text{D}_2\text{O} \sim 97\% \). All the parameters determined from the spectrum of the deutero-analog: \( \Delta \nu_{\text{AB}} = 5.0; J_{\text{AB}} = 1.4; J_{\text{AC}} = J_{\text{AD}} = 6.51 = 7.2; J_{\text{BC}} = J_{\text{BD}} = 6.51 = 15.1 \text{ Hz} \), 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-1H spectra of \( \text{T}_1\text{H} \) and \( \text{T}_1\text{D} \) were taken at the frequency 90 MHz (34°, Bruker HX-90 spectrometer) and 60 MHz (34°, Hitachi-Perkin-Elmer R-20 spectrometer). The ampoules with the substance to

* The authors of [14] initiated the addition of DBr to \( \text{CH}_2=\text{CCl}_2 \) with UV irradiation. After 18 h at 25°, the yield of the adduct was 62% (bp 134-135°, \( n^2_1 \) 1.5054).