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THE TEMPERATURE-DEPENDENT ^{1}H AND ^{13}C NMR SPECTRA OF 1,3,5-TRIMETHYL-2-DICHLORMETHYLBENZENE

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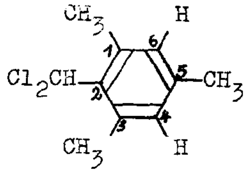
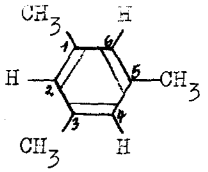
It was shown[2)] by ^{1}H nmr that in the ground-state of the title compound the proton of the dichlormethyl group is situated in the plane of the benzene ring. The height of the barrier to rotation about the Cl_2CH-C^2 bond was found to be $\Delta G_c^{\ddagger}$ = 14.0 ± 0.3 (-12°C, from $C^4\underline{H}$ and $C^6\underline{H}$) and 13.9 ± 0.2 kcal/mole (-1°C, from $C^1\underline{CH}_3$ and $C^3\underline{CH}_3$) in CS_2 solution[2)]. - We have now used ^{13}C nmr in order to test its capability in conformational analysis and chemical kinetics. Fourier-transformed ^{13}C spectra with a satisfactory signal-to-noise ratio were obtained at 22.63 MHz with a Bruker HX spectrometer, locked on the ^{19}F resonance of C_6F_6, a small quantity of which had been added to the solution (mole fraction 0.35) of **1** or **2**, respectively, in C_2Cl_4. 512 scans (0.4 sec) were accumulated, the pulse width being 50 usec. Protons were noise-decoupled.

Table: δ-Values for ^{13}C, corresponding to lower frequencies than that of internal tetramethylsilane (δ = 0). Conditions: See text.

1





2

1	-δ, +62°C	139.3, 139.3	133.1	130.5	68.5	21.0	20.2
	-δ, -31°C	139.1, 138.5	133.1, 132.7	131.8, 128.3	68.1	21.0	20.4, 20.0
	Assignments	C^2 C^5	C^1 C^3	C^4 C^6	Cl_2CH	$C^5\underline{CH}_3$	$C^1\underline{CH}_3$ $C^3\underline{CH}_3$
2	-δ, +33°C	137.2		127.0	-	21.2	
	Assignments	C^1, C^3, C^5		C^2, C^4, C^6	-	CH_3	

The assignments given for **1** are based upon the comparison of its δ-values with those of **2** [3](Table) and upon the observation that the signals at $\delta = -131.8$ and -128.3 form a broad hump when protons are off-resonance [4]decoupled, while the other four signals of aromatic carbon atoms remain sharp. Furthermore, four pairs of signals at lower temperatures (Table) change to four singlets at higher temperatures. In the cases of C^4/C^6 and $C^1\underline{C}H_3/C^3\underline{C}H_3$ we have been able to show that these changes represent true coalescences. From the chemical shift difference ($\Delta\nu$ = 73 Hz) between C^4 and C^6 and from the coalescence temperature (T_c = +12°C) we calculate $\Delta G_c^{\ddagger}$ = 13.8 ± 0.3 kcal/mole. Precisely the same result is obtained from $C^1\underline{C}H_3$ and $C^3\underline{C}H_3$ ($\Delta\nu$ = 10 Hz; T_c = -7°C). The same nmr sample was used for ^1H signal coalescence measurements; the barrier heights were $\Delta G_c^{\ddagger}$ = 13.8 ± 0.2 (-5°C, from $C^4\underline{H}$ and $C^6\underline{H}$) and 13.9 ± 0.3 kcal/mole (0°C, from $C^1C\underline{H}_3$ and $C^3C\underline{H}_3$)[5].

The difference $\Delta\delta$ = 3.5 for $\underline{C}^4H/\underline{C}^6H$ is surprising when the small values of 0.4 for C^1/C^3 and of 0.4 for $C^1\underline{C}H_3/C^3\underline{C}H_3$ are taken into account. The results from ^1H nmr were $\Delta\delta$ = 0.14 for $C^4\underline{H}/C^6\underline{H}$ and $\Delta\delta$ = 0.35 for $C^1C\underline{H}_3/C^3C\underline{H}_3$ at -31°C.

The above findings show that the same conformational conclusions, e.g. for the ground-state of **1**, are feasible from both methods. Unlike the present case, the complementary application[6] of ^1H and ^{13}C nmr may be useful if the chemical shift differences between corresponding signals differ considerably for the two nuclei.

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1) To whom inquiries should be addressed.

2) A.Mannschreck and L.Ernst, Chem.Ber. **104**, 228 (1971) and unpublished results.

3) Cf. P.C.Lauterbur, J.Amer.Chem.Soc. **83**, 1838 (1961).

4) E.Wenkert, A.O.Clouse, D.W.Cochran, and D.Doddrell, J.Amer.Chem.Soc. **91**, 6879 (1969).

5) $|\Delta S^{\ddagger}|$ for compounds similar to **1** is small; see, for example, H.G.Gyulai, B.J.Fuhr, H.M.Hutton, and T.Schaefer, Can.J.Chem. **48**, 3877 (1970).

6) Cf. O.A.Gansow, J.Killough, and A.R.Burke, J.Amer.Chem.Soc. **93**, 4297 (1971).