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INTRINSIC DIASTEREOISOMERISM IN ^{13}C SPECTRA. A STUDY OF THE ROTAMERS OF 2,3-DIBROMO-2-CHLORO-3-METHYLBUTANE

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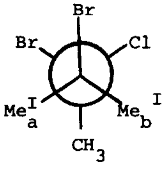
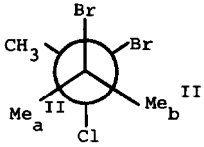
Examination of low temperature (-60°) ^{13}C n.m.r. spectra of 2,3-dibromo-2-chloro-3-methylbutane (1) shows that intrinsic non-equivalence may be considerable for ^{13}C nuclei. Previous work has shown that although intrinsic diastereoisomerism is usually small for ^{1}H spectra[1] it may contribute significantly to the spectra of ^{19}F nuclei.[2] The study of conformational preference in molecules presumes that the intrinsic contribution to chemical shift non-equivalence is small[3] and as ^{13}C spectra are now being used for this purpose[4] it became necessary to investigate whether this presumption was correct.

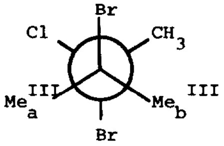
The ^{1}H spectra of (1) in CCl_4, $CDCl_3$, CH_2Cl_2 and CS_2 show the geminal methyl groups to be non-equivalent by ca. 0.04 ppm at 30°. Spectra at -60° in these solvents were interpretable in terms of slow isolation around the C_2-C_3 bond[5] and showed signals for the three rotamers I, II and III. The observation of three rather than six absorptions for the geminal methyl groups is again consistent with a low contribution of intrinsic diastereoisomerism to ^{1}H spectra, i.e. $\delta\ Me_a^{I} \simeq \delta\ Me_b^{III}$ etc.



I



II



III

^{13}C N.m.r. spectra at ambient temperature showed the geminal methyls to be non-equivalent by values of 0.65, 0.90 and 0.68 ppm in $CDCl_3$, CH_2Cl_2 and CS_2 respectively. Spectra at -60° showed three pairs of absorptions in each solvent, thus indicating that intrinsic diastereoisomerism was significant for ^{13}C spectra. The rotamers were present in ratio ca. 1(I) : 3(II) : 5(III). Structure and chemical shift assignments were made using previous techniques[6] and led to the tabulated values.

Chemical Shift Values for the Geminal Methyl Carbons in I[+]

Solvents	I_a	I_b	II_a	II_b	III_a	III_b
$CDCl_3$	29.25	29.17	28.25	32.63	32.25	30.90
CH_2Cl_2	29.75	28.94	28.43	33.58	32.35	31.59
CS_2	30.12	29.21	28.71	33.15	32.60	31.32

[+] Measured downfield from TMS for 2.0 M solutions using a Bruker WH 90 spectrometer operating at 22.63 MHz. Spectra did not vary significantly for solutions 0.5 - 2.0 M in $CDCl_3$.

The intrinsic diastereoisomerism is thus calculated to be 0.98 ($CDCl_3$), 1.17 (CH_2Cl_2) and 0.75 (CS_2) ppm using the method of Raban.[2] These figures suggest that the intrinsic contribution is dominant in the overall ^{13}C chemical shift non-equivalence of the geminal methyl groups of (I) at ambient temperature.

Acknowledgments

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