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DEUTERIUM ISOTOPE EFFECT IN ^{1}H CHEMICAL SHIFT OF BENZENE-d_1

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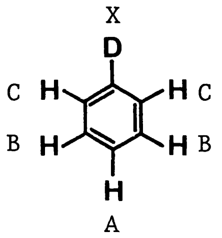
90 MHz ^{1}H-NMR spectrum of liquid benzene-d_1 has been measured and completely analysed as an AB_2C_2X (X=D, I=1) system. The deuterium isotopic shifts relative to internal benzene, $\Delta_A = -1.4$ ppb, $\Delta_B = -1.3$ ppb and $\Delta_C = +0.3$ ppb, have been determined.

60 MHz ^{1}H-NMR spectrum of benzene-d_1 obtained by Abraham and Bernstein1) appears to be a symmetrical triplet spacing of 0.55 Hz. The separation of the triplet lines was interpreted by the average of three ^{1}H-^{2}D coupling constants, $1/5(^5J_{AX} + 2\ ^4J_{BX} + 2\ ^3J_{CX}) = 0.57$ Hz.2) Since then, this simple averaging method has been frequently used for the analysis of the spectrum of deuterio-compound. However, there still remains uncertainty, in particular, in the relative intensity of each peak and numerical value of the deuterium isotopic shift.



We previously reported on the unsymmetrical spectrum at 90 MHz.3) And lately, the extremely accurate measurements have been made on a Hitachi R-22 high resolution nmr spectrometer (CW mode, 35 °C), using TMS as the internal lock signal. The representative pattern of the neat sample shown in Fig.1(a) was obtained with a slow sweep of 20 Hz/4000 sec. The measurement was repeated 20 times in order to ascertain the reproducibility. Taking the deuterium isotopic shifts into consideration, we analysed the spectrum completely, with a Hitachi micro computer, Basic Master MB 6881 (32 K). Fig.1(b) shows the best fitting pattern, which was calculated with the assumption that the intra-molecular isotopic shifts are $\delta_A - \delta_B = 0.1$ ppb and $\delta_B - \delta_C = 1.6$ ppb, and that the order of the shifts is δ_A, δ_B, δ_C from the downfield to the upfield. ^{1}H-^{1}H coupling constants employed were those determined by Read *et al.*,4) and ^{1}H-^{2}D coupling constants were derived from ^{1}H-^{1}H coupling constants and $\gamma_H/\gamma_D = 6.5144$.

The inter-molecular isotopic shifts have been found from the analysis of the spectrum on the mixture of benzene-d_1 and benzene, as $\Delta_A = -1.4$ ppb, $\Delta_B = -1.3$ ppb and $\Delta_C = +0.3$ ppb from benzene, with an accuracy of about ± 0.2 ppb. The half height widths of each peak of benzene-d_1 and that of benzene were 0.23 Hz and 0.19 Hz, respectively. Negative values designate downfield shifts and positive value does an upfield shift. Negative values should be noted as the uncommon example. These values of the long range deuterium isotopic shifts are very small, but important for the interpretation of the fine structure of ^{1}H-NMR spectrum of the aromatic deuterio-compound.

Although the simple averaging method proposed by Abraham and Bernstein$^{1)}$ is available in 1-st order analysis of the NMR spectrum of deuterio-compound, the present result leads us to analyse completely for the investigation on the isotope effect, regardless of the relative magnitudes of the ^{1}H-^{2}D coupling constants.

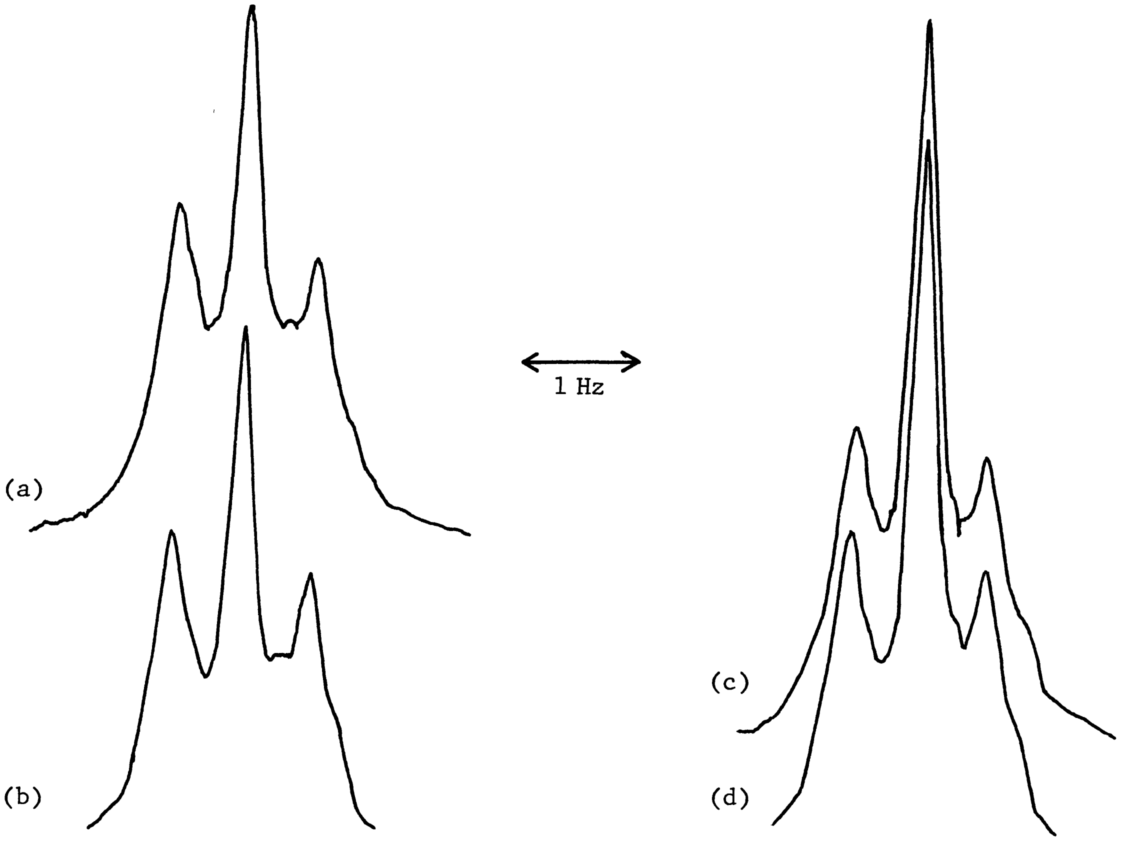


Fig.1. 90 MHz ^{1}H-NMR spectra of benzene-d_1; (a) observed, (b) calculated, (c) observed on the mixture of benzene-d_1 and benzene, (d) calculated on the concentration of benzene-d_1 and benzene of 8.31 : 1.

References

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