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# ON THE MAGNETIC NON-EQUIVALENCE OF METHYLENE PROTONS IN SOME PROPANE DERIVATIVES, AND ITS VARIATION WITH SOLVENT AND TEMPERATURE

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## ABSTRACT

The magnetic non-equivalence, $\delta$ab, of methylene protons in 1,2-disubstituted and 1,2,3-trisubstituted propanes (same substituent) shows a marked dependence on solvent and temperature that allows a correlation with conformational equilibrium. Results indicate that symmetry is a necessary, but not a sufficient, condition for observation of $\delta$ab. Factors that affect rotamer population such as medium, temperature, and nature of substituents, contribute substantially to the magnitude of $\delta$ab.

## INTRODUCTION

It is well known that methylene protons in molecules possessing free rotation about skeleton chemical bonds can exhibit magnetic non-equivalence if no plane of symmetry passes through the methylene carbon and adjacent carbon [1]. Under these conditions, the three fields experienced by each proton in the three interconverting staggered rotational isomers are different. The rotationally-averaged chemical shifts $<\nu_a>$ and $<\nu_b>$ for protons a and b are

$$<\nu_a> = X_1\nu_1{}^a + X_2\nu_2{}^a + X_3\nu_3{}^a \qquad (1)$$

$$<\nu_b> = X_1\nu_1{}^b + X_2\nu_2{}^b + X_3\nu_3{}^b \qquad (2)$$

where subscripts indicate rotamers, superscripts the methylene protons, and $X$ the mole fraction of the rotamer. This condition, however, although necessary for observation of non-equivalence, is insufficient, *unless* it is coupled with another condition related to the imbalance in rotamer populations. This detail and the relative importance of the two conditions mentioned, namely the symmetry and averaging, has been a matter of controversy in the literature. Roberts and co-workers [2] emphasized the importance of the residence time of the various conformers, whilst Gutowsky

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[3], and Waugh and Cotton [4] stressed the role of asymmetry. In the present work, data of magnetic non-equivalence of methylene protons in 1,2-disubstituted and 1,2,3-trisubstituted propanes (same substituents) and their dependence on solvent and temperature are reported.

## EXPERIMENTAL

### *Materials*

1,2,3-Trichloro- and 1,2-dichloropropane were prepared by treatment of 3-chloro-1,2-propanediol and 1,2-propanediol with thionyl chloride. 1,2-Diacetoxypropane was prepared by treatment of 1,2-propanediol with acetyl chloride. 1,2,3-Tribromopropane was prepared by addition of bromine to allyl bromide. 1,2-Dibromopropane and 1,2,3-triacetoxypropane were obtained commercially and purified by vacuum distillation.

### *Measurements of NMR spectra*

The NMR spectra of all compounds were recorded using a Varian A60D NMR spectrometer system, equipped with a variable temperature unit. All samples were used at a concentration of 5% (w/w).

## DISCUSSION

There is some reservation in the literature [1] about associating solvent- and temperature-dependence of magnetic non-equivalence with changes in conformational population. The reasoning follows from a consideration of the changes in the magnetic non-equivalence of methylene protons of 2-carboxypropene, where no rotation about the double bond is possible. In fact, this effect is a result of the two protons being anisotropically affected by solvent—solute interaction. 1,2-Disubstituted propanes are more convenient for such consideration. The methyl protons in these compounds are not affected by the conformational equilibria, and the variation in chemical shift with solvent reflects the solvent—solute interaction. Results obtained in this laboratory indicate that, except for benzene, all solvents show little effect on the chemical shifts of methyl protons compared to the shifts resulting from other protons associated with the conformational equilibrium.

Inspection of Fig. 1 reveals that, except for some non-bonded interactions the following equalities should hold

$$\nu_1^a = \nu_2^b \qquad (3)$$

$$\nu_2^a = \nu_3^b \qquad (4)$$

$$\nu_3^a = \nu_1^b \qquad (5)$$

In the special case where $X_1 = X_2 = X_3 = 1/3$, combination of eqns. (1)—(5) leads to $\langle\nu_a\rangle - \langle\nu_b\rangle = \delta ab = 0$.

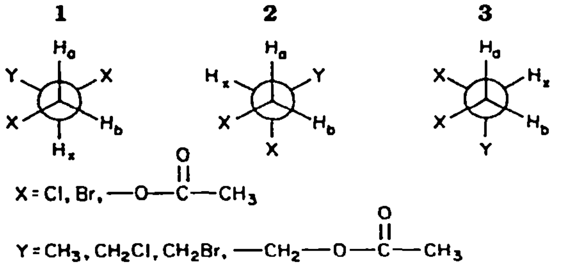

Fig. 1. The three interconverting staggered conformers of 1,2-di- and 1,2,3-tri-substituted propanes.

Non-bonded interactions of the type shown above are expected to contribute very little to magnetic non-equivalence of methylene protons and this minor contribution, if it exists, would give rise to an inherent magnetic non-equivalence of methylene protons attached to an asymmetric centre, as described by Gutowsky [3].

In order to prove this assumption, $\delta$ab for the methylene protons in a molecule with a high degree of asymmetry, 1,2-dichloropropane, has been varied by changing the solvent and temperature. In non-polar solvents the spectrum of the compounds showed a clear $ABCX_3$ system. However, in dimethyl sulphoxide and acetonitrile at 38°C and in acetone at −20°C, the eight lines constructing the $AB$-part collapsed to a doublet. This experiment supports the view that magnetic non-equivalence is a consequence of imbalance in rotamer populations observable in compounds of certain symmetry.

### *Variation of $\delta ab$ with solvent and temperature*

Figure 2 and Table 1 show that $\delta$ab decreases with increasing dielectric constant of the medium. This is to be expected since an increase in the populations of polar structures **2** and **3** would lead to a decrease of the imbalance in the rotamer populations and hence to a reduction in the magnetic non-equivalence of the two protons. Similar results have been obtained as a consequence of the variation of vicinal coupling constants $J$ac and $J$bc with temperature and solvent [5, 6]. The rate of decrease conforms to the polarity of the carbon—substituent bond. The size of a substituent should also have a definite effect since it is very difficult to stabilize rotamer **2** with three bulky substituents *gauche* to each other.

Table 2 gives the change in $\delta$ab on decreasing the temperature from 38°C to −20°C for solutions in acetone and in carbon tetrachloride. Lowering the temperature favours the conformer with less steric strain and, in addition, increases the dielectric strength of the solution. The magnitude of the increase is proportional to the polarity of the solution. For 1,2-diacetoxypropane, which is weakly polar, an increase in the non-equivalence arises because conformer **1** is favoured. For 1,2-dibromopropane there is a considerable increase in $\delta$ab on going from acetone to carbon tetrachloride as solvent. Evidently, in the strong polar solvent, acetone, the stabilization of

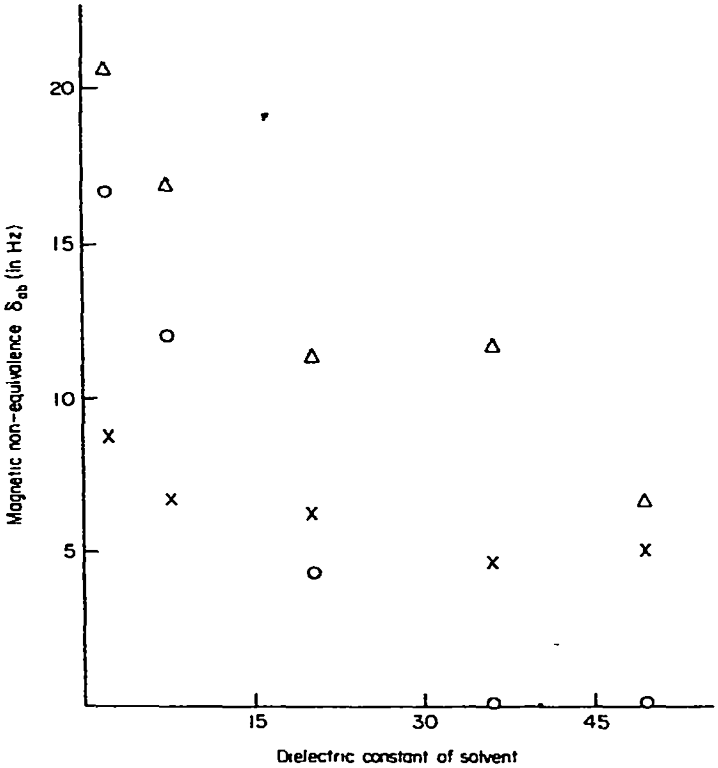

Fig. 2. Magnetic non-equivalence as a function of dielectric constant of solvent; △, 1,2-dibromopropane; ○, 1,2-dichloropropane; ×, 1,2-diacetoxypropane.

TABLE 1

Solvent-dependence of $\delta ab$ (Hz) for 1,2-disubstituted propanes at 38°C

| Compound | Solvent | | | | |
|---|---|---|---|---|---|
| | Carbon tetrachloride | Chloroform | Acetone | Acetonitrile | Dimethyl sulphoxid |
| 1,2-Dibromopropane | 20.8 | 19.6 | 11.4 | 11.6 | 6.7 |
| 1,2-Dichloropropane | 16.8 | 12.0 | 4.3 | 0.0 | 0.0 |
| 1,2-Diacetoxypropane | 8.8 | 6.7 | 6.2 | 4.6 | 5.1 |

the polar and sterically less-favoured conformers 2 and 3 balances the steric factor. This is more accentuated for 1,2-dichloropropane owing to the increased polarity and decreased bulkiness of the substituents. The decrease of $\delta ab$ in acetone indicates that stabilization of conformers 2 and 3, arising from the increase of dielectric strength with the decrease in temperature, is the main contributory factor.

TABLE 2

Temperature-dependence of $\delta ab$ (Hz) for 1,2-disubstituted propanes

| Compound | Solvent (temperature) | | | |
|---|---|---|---|---|
| | Acetone (38°C) | Acetone (−20°C) | Carbon tetrachloride (38°C) | Carbon tetrachloride (−20°C) |
| 1,2-Dichloropropane | 4.31 | 0.0 | 16.8 | 17.9 |
| 1,2-Dibromopropane | 11.4 | 12.1 | 20.8 | 23.8 |
| 1,2-Diacetoxypropane | 6.2 | 9.6 | 8.8 | 11.7 |

### *Effect of symmetry on $\delta ab$*

Table 3 compares $\delta ab$ for compounds belonging to two different symmetry classes that fulfil the requirement for asymmetry. Whilst $\delta ab$ decreases on going from 1,2-disubstituted to 1,2,3-trisubstituted propanes for Cl and Br substituents, the magnetic non-equivalence increases slightly on going from 1,2-diacetoxy- to 1,2,3-triacetoxy-propane. It is therefore reasonable to conclude that, besides symmetry, other factors related to the nature of the substituents contribute to the magnitude of $\delta$ ab.

TABLE 3

$\delta ab$ (Hz) for 1,2-disubstituted and 1,2,3-trisubstituted propanes, measured in chloroform at 38°C

| Compound | $\delta ab$ | Compound | $\delta ab$ |
|---|---|---|---|
| 1,2-Dichloropropane | 12.0 | 1,2,3-Trichloropropane | 0.0 |
| 1,2-Dibromopropane | 19.6 | 1,2,3-Tribromopropane | 5.0 |
| 1,2-Diacetoxypropane | 6.7 | 1,2,3-Triacetoxypropane | 8.4 |

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