STUDY OF INTRAMOLECULAR MOTION BY NMR OF ORIENTED MOLECULES

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ABSTRACT

After a short comparison of conformational studies in isotropic liquids with studies in oriented solvents the typical problems and limitations of the latter are discussed and illustrated with applications in *o*-substituted toluenes, toluene, benzaldehyde, salicylaldehyde, phenol and aniline. Possible further developments are mentioned.

1. INTRODUCTION

Compared with nmr studies of conformational problems in isotropic liquids in which dynamic averages of chemical shifts and indirect couplings are observed, the corresponding studies in partially-oriented molecules seem to have a distinct advantage: there exists a simple theory for the observed direct coupling which is being averaged. It is directly related to the variable molecular geometry and orientation. On the other hand there are certain typical limitations and problems:

1. Quite generally from known geometries of conformers and observed direct couplings as weighted averages over the path of the motion, the conformer concentration cannot be determined. The reason is that the concentrations p_i and the degrees of orientation S_i always appear as one factor p_iS_i which cannot be separated. If, on the other hand, the concentrations of the various conformers are known and the number of observed direct couplings exceeds the number of parameters defining the molecular orientation and the relative nuclear coordinates, in principle, the molecular shape as well as conformational details may be derived.

2. A second general problem in such studies arises from a possible rate competition among three different processes: one for the nmr experiment, one for the intramolecular motion, and one for the reorientation of the molecule in the liquid crystal. The slow rate of the nmr experiment actually contributes to the limitation mentioned above, i.e., the observed average not allowing a determination of concentrations. The other two rates affect the spectra via an apparent symmetry or asymmetry. For example the molecule benzaldehyde may be studied for the purpose of determining whether it has a chance to reorient itself after each turn of the substituent from one planar form to another. If it reorients, the molecule displays asymmetry and three parameters are necessary for a definition of its orientation. If not, two are sufficient.

3. A third difficulty arises if a change of temperature is necessary. The

reasons are first, that the range of temperature in which the liquid crystal solution remains nematic is limited; and secondly, the molecular orientation, and with it the direct couplings, vary with temperature.

In order to study the possibilities and limitations in conformational studies with oriented molecules, our nmr group at Basel analyzed the spectra of a series of compounds as discussed in the following section.

2. APPLICATIONS

2.1 *O*-substituted toluenes

It is obvious that most of the above mentioned difficulties may be avoided if the studies are limited to intramolecular rotation in simple *n*-fold potentials. These are approximately realised for hindered methyl rotation in *o*-substituted toluenes and toluene itself. A typical spectrum is shown in Figure 1.

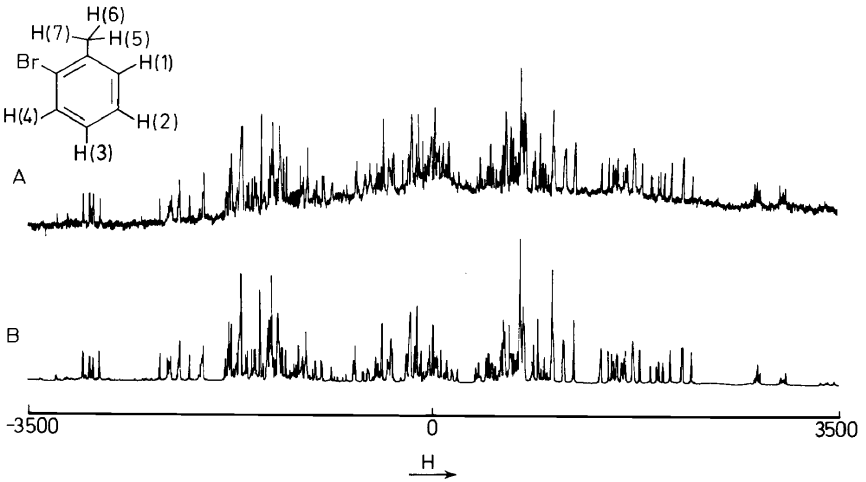

Figure 1. Observed (A) and calculated (B) proton magnetic resonance spectrum of *o*-bromotoluene partially oriented in the nematic phase of *N*-*p*-ethoxybenzylidene-*p*-butylaniline. Concentration: 22 mole %; temperature 28°C, frequency 56.4 MHz.

The analysis of the problem proceeds as follows:

1. The spectrum is analyzed by computer.

2. The probability distribution of the rotating group with respect to rotational angle is obtained from the Schroedinger equation after inclusion of the cosine potential function, solution of the resulting Mathieu equation for the eigenvalues, determination of eigenfunctions and finally consideration of the Boltzmann distribution of the rotating groups among the various states.

3. The probability distribution is introduced into a further computer program which iterates on molecular geometry and determines an rms error of the fit. By variation of potential height and position of minimal energy the smallest rms error corresponding to the final solution is determined.

This procedure turned out to be quite efficient and the following results for

the barrier heights were determined:

o-chlorotoluene[1]	1.2+0.6 kcal mole^{-1}
o-bromotoluene[2]	0.9±0.6 kcal mole^{-1}
o-iodotoluene[2]	1.8±0.6 kcal mole^{-1}

In all three cases the position of minimal energy was with the substituent atom staggered to the methyl group.

It should be pointed out that contrary to normal nmr this measurement is particularly sensitive to small barriers of the order of 0–4 kcal mole^{-1}. The variation in the most sensitive direct coupling (from the *o*-proton to the methyl protons) between free rotation and a barrier height of 4 kcal mole^{-1} is approximately 40 Hz, whereas it is 50 Hz between free rotation and stable rotamers.

2.2. Toluene

The case of toluene[3] proved to be insensitive to the barrier height. The variation of the most sensitive direct coupling between free rotation and stable rotamers is only 2 Hz. The main reason for this insensitivity must be the sixfold symmetry of the problem. Whereas the direct coupling in *o*-substituted toluenes (period of 120°) varies appreciably with the rotation angle (100 Hz) of the methyl group, the variation in toluene (period of 60°) is very much reduced (4 Hz). The barrier height could not be determined. However, the molecular geometry was obtained with considerable precision. The potential minimum seems to be with a C—H bond in a plane perpendicular to the benzene plane.

2.3. Benzaldehyde

Whereas toluene and *o*-substituted toluenes are overdetermined or just determined by the number of observable direct couplings, benzaldehyde[4] is underdetermined. Due to the aldehyde group rotation only 9 couplings are available. However, there are 10 relative coordinates and 3 orientation parameters unknown. Consequently certain geometrical assumptions had to be made.

In principle, various models seemed reasonable. These are: free rotation of the aldehyde group; an observed average of two forms with the aldehyde group in the benzene plane, with or without reorientation of the molecule; and finally, rather improbable stable forms with the aldehyde group perpendicular to the ring plane, again with or without reorientation. The experimental data allowed us to discard the last two cases as well as free rotation on the basis of unreasonable resulting molecular geometries. The barrier height was not obtained nor was it possible to confirm or exclude molecular reorientation between successive internal rotations.

2.4. Salicylaldehyde

For benzaldehyde as well as salicylaldehyde[5] the shape of the hindering potential may be no longer a simple cosine function. For the latter there arises the additional problem of the influence of the intramolecular hydrogen bond.

The analysis of the spectrum first of all showed that direct coupling to the hydrogen bonded proton is observable and that consequently at least the structure of the hydrogen bond may be studied. Again the height and type of the barrier to intramolecular rotation could not be determined. However, the observed spectrum could only be explained on the basis of a nonplanar molecular structure in which the carbonyl and hydroxyl groups are twisted by approximately 15° so as to place their protons on the same side of the ring plane. An alternative but rather improbable solution could also be obtained in which the potential is very flat out to a range of ±30° from the plane so that a large proportion of nonplanar species may exist.

2.5 Phenol

In phenol[6] as in benzaldehyde certain possibilities like e.g. free rotation of the substituent could easily be disproved on the basis of the observed spectrum. Again the question arose whether the molecule reorients in the liquid crystal after each hydroxyl rotation, i.e. whether 2 or 3 orientation parameters are necessary for the analysis. It turned out that 3 were required so that here for the first time reorientation could definitely be detected.

Another peculiarity of this molecule is the unusual orientation which was found with the principal axis in the plane of the ring but on the opposite side of the oxygen from the hydroxyl proton. This deviation from the normal behaviour (main axis along the largest feature of the molecule) may perhaps be attributed to intermolecular hydrogen bonding of phenol to the liquid crystal.

2.6. Aniline

This molecule resisted all the attacks in that no good spectrum could be obtained. The explanation for this peculiar behaviour may be seen on *Figure 2.*

The spectrum of 2,4,6-tribromoaniline[7] appears to consist of two widely separated symmetrical triplets. The resonance of the amine protons is broadened out of sight in the spectral centre while the ring proton lines are reasonably sharp. The broadening must be attributed to a direct coupling of protons to the quadrupole relaxed ^{14}N nucleus. Consequently the 'bad' spectrum of oriented aniline must be explained as an intermediate type of spectrum in which some direct couplings are averaged out to various degrees while some are still fully observable.

3. FURTHER DEVELOPMENTS

The cases discussed in the preceding section show that a further development in conformational studies by nmr of oriented molecules is rather difficult. In only one type of molecule the original aim, i.e. a detailed study of the intramolecular motion, has really been achieved. In all the others the available information was limited by the various difficulties pointed out in the introduction. Further molecules like e.g. *n*-propyl chloride are presently being studied; the results, however, do not yet seem to be promising.

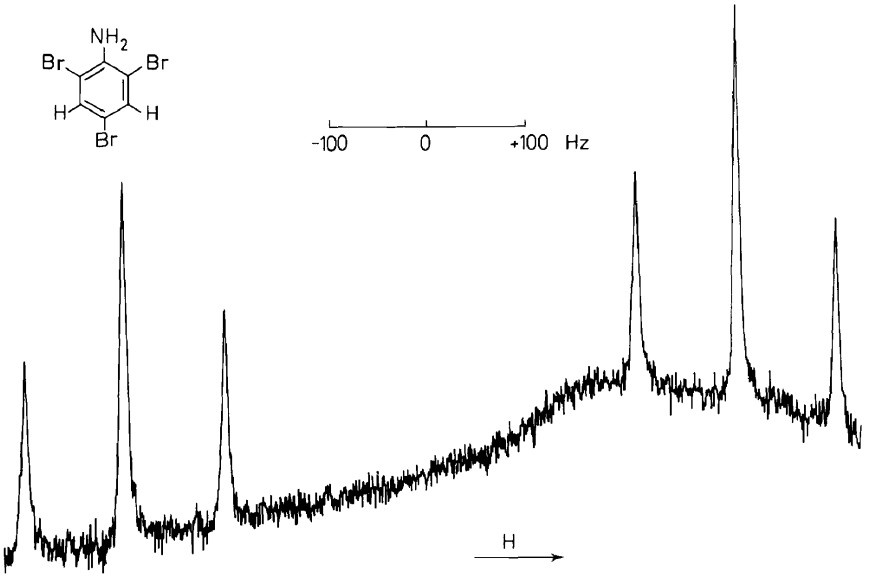

Figure 2. Proton magnetic resonance spectrum of partially oriented 2,4,6-tribromoaniline.

REFERENCES

[1] P. Diehl, P. M. Henrichs and W. Niederberger, *Mol. Phys.* **20**, 139, (1971).
[2] P. Diehl, P. M. Henrichs, W. Niederberger and J. Vogt, *Mol. Phys.* **21**, 377, (1971).
[3] P. Diehl, H. P. Kellerhals and W. Niederberger, *J. Magn. Resonance* **4**, 352, (1971).
[4] P. Diehl, P. M. Henrichs and W. Niederberger, *Org. Magn. Resonance* **3**, 243, (1971).
[5] P. Diehl and P. M. Henrichs, *J. Magn. Resonance* **5**, 134, (1971).
[6] P. Diehl and P. M. Henrichs, *Org. Magn. Resonance* **3**, 791, (1971).
[7] P. M. Henrichs, unpublished results.